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Löwdin Atomic Charges for Modeling Long Range Deuterium Isotope Shifts in C–13 NMR Spectra of Binuclear Aromatic Compounds[a]

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An approach for modeling long range deuterium isotope effects on C–13 chemical shifts, based on *ab initio* calculations of the differences of atomic charges between parent and deuterated molecules, is proposed. The total atomic charges were calculated for a series of molecules consisting of two benzene rings linked directly or *via* different groups, the so called binuclear aromatic molecules: biphenyl, *trans*-stilbene, *cis*-stilbene, diphenylacetylene, diphenylbutadiene and their 4-deuterated derivatives. The basis sets used were: STO-3G, 6-31G, 6-31G** and MIDI. The deuteration site, *i.e.* C–D bond was simulated by the shortening of the corresponding C–H bond length by 0.012 Å or by the reduction of CCH in-plane or out-of-plane bending angle by 1.3° and 2°, respectively. Calculations were performed both for the X-ray geometries and 6-31G fully optimized geometries. The charge differences from Löwdin but not from Mulliken population analysis, calculated with 6-31G, 6-31G** and MIDI basis sets, showed good correla-

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[a] Dedicated to Professor Per-Olov Löwdin, a great man and quantum theory scientist.

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tion with the measured longrange deuterium isotope effects on C–13 chemical shifts of C-atoms, five, six, seven, eight, ten and twelve bonds away from the site of deuteration. This correlation holds only for bond shortening but not for bending angle changes, which corresponds to the predominance of stretching over bending mode contributions to isotope effects. The vibrational analysis (6-31G) revealed no coupling of C–D stretching with the vibrations of remote C-atoms. Therefore, we assume that the symmetry breaking due to unsymmetrical deuterium substitution produces a small electric dipole moment by an unbalance in the normal vibrations which in turn polarizes π-electrons, giving rise to charge changes throughout the molecule. Calculated charge redistribution due to deuterium, experimentally also observed by microwave spectroscopy, might induce long-range deuterium isotope effects on C–13 chemical shifts in agreement with the postulated C–C π-bond polarization contribution to C–13 chemical shifts.

INTRODUCTION

In recent years, calculations of C–13 magnetic shieldings have been significantly improved, giving an average precision of *ca.* 5 ppm, even for medium size molecules. However, this is still beyond the level needed for long range deuterium isotope effects (LRDIE), *i.e.* the effects through more than four bonds, to be even roughly calculated. The reasons are the low magnitude of LRDIE, usually in the range from 1 ppb to 15 ppb per deuterium atom, and complex vibrational patterns in large molecules in which these effects have been observed. In fact, for most polyatomic molecules in which LRDIE were found, the normal coordinates and force fields are not known and the role of different vibrations in influencing isotope effects on nuclear shielding has not yet been resolved. As a consequence, a full theoretical treatment of LRDIE is currently not possible and theoretical approaches using semi-empirical elements may be helpful in understanding LRDIE. The isotope effects on NMR chemical shifts arise from different vibrational and rotational averaging of nuclear shielding in isotopomers as a result of different zero-point vibrational levels for bonds to different isotopes, *e.g.* C–H and C–D bonds, and anharmonicity of the vibrational potential.[1] Thus, small changes in average bond lenghts and average bond angles on isotopic substitution may contribute to isotope effects.[2] In fact, these changes may give rise to electron redistribution throughout the deuterated molecule, which may contribute to the LRDIE.[2,3] There are several experimental reports that the C–D bond is somewhat shorter than the C–H bond. In the gas phase,[4] the electron diffraction on CH_4 and CD_4 revealed a reduction of the bond length of 0.004 Å, while for 1-D-benzene dissolved in a liquid crystal phase[5] the shortening found was as large as 0.020 Å. In addition, the observation of pure rotational spectra of monodeuterated-acetylene[6] and -benzene[7] (dipole moments of the order of 10^{-2} D) proved that the electric charge distribution of a molecule is slightly changed upon isotopic substitution. The atomic charge is not rigorously defined in quantum mechanics.[8] In spite of that, the concept of charge is widely used since it provides semiquantitative information on a number of molecular properties and enables molecular simulations and energy minimizations.[9,10] The shortening of a specific C–H bond and calculation of the accompanying changes of the Mulliken charges by semiempirical INDO and CNDO/2 methods in naphthalenes and azulenes could not reproduce deuterium isotope effects through more than one bond.[11] However, for some small aliphatic molecules, *e.g.*, acetone, 2-propyl cation, *etc.*, the same procedure but with *ab initio* calculations at the STO-3G level gave fairly good values of two-bond deuterium isotope effects on C–13 shifts, although it was emphasized that such calculations had failed for many other simple molecules.[12] As far as we know, two-bond isotope effects are the longest deuterium effects on C–13 shifts ever calculated until now. The relationships between C–13 chemical shifts and C-atomic charges are well documented although it was shown that the full generalization is not possible since other important effects exist.[13] However, it was found that in a series of closely related compounds the change of total magnetic shielding of atomic nuclei is nearly that of the local paramagnetic term, giving a justification for relationships between chemical shifts and local atomic populations in such cases.[14] The isotopically labelled molecules are the most closely related of all molecules, since there is no gross electron difference between them. Therefore, charge-shift relationships might be more reliable for isotopomers than for substituted molecules or molecules with different ring sizes where electronic and structural differences may have a significant effect. Taking the above into account, we have probed the LRDIE by *ab initio* calculations of the differences in atomic charges between the parent and deuterated molecules. The C–D bond was modeled by the shortening of the corresponding C–H bond length and/or variation of the CCH in-plane and out-of-plane bending angles at the site of deuteration. The former simulates the deuterium isotope effect upon the stretching, while the latter simulates the effect upon the bending modes. Since charges from the Mulliken population analysis have been shown to be unsatisfactory for probing the deuterium long range isotope effects,[11,12] and some other properties,[15] we have investigated the merits of charges from the Löwdin population analysis as well.

The longest range deuterium isotope effects were observed in binuclear aromatic compounds consisting of two benzene rings linked directly or *via* different groups.[16] We studied *trans*-stilbene (tSB) as a model molecule, where the benzene rings are connected with an ethylenic group, and related *cis*-stilbene (cSB), biphenyl (BP), diphenylacetylene (DPA), and 4'-methyl-diphenylbutadiene (DPB) (experimental data for the DPB without methyl group are not available) and their 4-deuterated isotopomers. The structural formulas and enumeration of C-atoms in BP, tSB, and DPB are displayed in Figure 1.

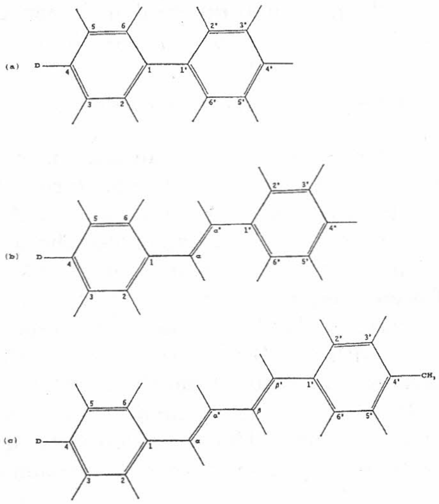

Figure 1. Structural formulas and enumeration of C-atoms in 4-D-BP (a), 4-D-tSB (b) and 4-D-4'-Me-DPB (c).

MEASUREMENTS

For all compounds, except for 4'-methyl-diphenylbutadiene,[16] we have performed C–13 NMR measurements on Varian XL–400 and Varian VXR–500S NMR spectrometers, operating at 101 and 125 MHz for C–13 nuclei, respectively. The concentrations of samples dissolved in deuterated acetone solution, measured at 20 and 26 °C, were 0.1–0.2 mol/L. The deuterium isotope effects were determined from different mixtures of deuterated and undeuterated species. The digital resolution of measurements was 0.67 ppb. High homogeneity of magnetic field was attained, as well as control of sample concentration and temperature, since isotope effects may be concentration, solvent and temperature dependent.[17] In principle, detection of isotope effects of a magnitude equal or greater than double the value of digital resolution could be possible if there is no signal broadening and C–D couplings. Other experimental details will be published elsewhere.[18]

COMPUTATIONAL METHODS

The *ab initio* calculations were performed using the GAUSSIAN 92 program.[19] Both full optimized geometries and harmonic frequencies were calculated with a 6–31G basis set. The charges were calculated by the GAMESS program[20] with STO-3G, 6-31G, 6-31G** and MIDI basis sets.[21] The GAMESS program calculates both the Mulliken and Löwdin population analysis. X-ray geometries were taken from the Cambridge Structural Database System (CSDS).[22] For all deuterated molecules, the C–D bond was simulated by the reduction of the corresponding C–H bond by 0.012 Å and, after that, calculations of charges were performed (the 0.012 Å bond reduction value is the mean value of shortening estimated from different spectroscopic measurements[4,5]). In 4-D-tSB, charges were also calculated for the out-of-plane CCH bending angle change of 2° and in-plane CCH bending angle change of 1.3°. Both values were assumed on the basis of theoretical prediction which postulates an approximately 1% change of some molecular property on isotopic substitution.[23] The dependence of charges upon the molecualr dihedral angle between benzene rings and ethylenic group was, in 4-D-tSB, calculated for angles 6°, 20°, 45° and 90° as well.

RESULTS AND DISCUSSION

Table I displays the differences of the total atomic charges between tSB and 4-D-tSB for C-atoms five to ten bonds away from the deuterium atom, calculated with different basis sets using the X-ray geometry with a 0.012 Å C–H bond reduction. The minus sign of the measured isotope shifts denotes the deshielding effect, *i.e.* a decrease of the electron density at nucleus, and to adapt to this sign convention, we denoted the decrease of atomic electron charge with a minus sign as well. For all basis sets used, the correlation of Mulliken charge differences (M) with measured isotope effects is very poor (with 6-31G r^2 = 0.006 while with MIDI r^2 = 0.77). In contrast, the charge differences calculated from the Löwdin population analysis (L) with 6-31G, 6-31G** and MIDI, but not the minimal basis set STO-3G, correlate well with the experimental LRDIE. Since 6-31G has given virtually the same results as the larger basis sets, we have used it in further calculations because of its lower computational cost.

In Figure 2, the correlation between LRDIE and the differences of L and M is displayed. The correlation coefficient, r^2, for Löwdin charges calculated with 6-31G

TABLE I

Mulliken (M) and Löwdin (L) charge differences (in 10^{-6} a.u.) calculated for 4-deutero-*trans*-stilbene with different basis sets using X-ray geometry and C-H bond reduction of 0.012 Å.

Atom	N[a]	STO–3G		MIDI		6–31G		6–31G**		LRDIE[b]
		M	L	M	L	M	L	M	L	
α	5	22	33	–4	–18	14	–18	4	–16	–9
α'	6	–45	–62	18	26	10	28	11	25	10
1'	7	–7	–11	–9	–9	–11	–11	–10	–10	–2.8
2'	8	–10	–12	7	7	6	7	5	6	0[c]
6'	8	–9	–11	6	6	7	8	7	7	0[c]
3'	9	0	0	0	1	1	2	–1	3	0
5'	9	–1	–1	0	1	1	2	0	2	0
4'	10	–9	–13	7	11	7	12	6	12	2.8

[a] Number of intervening bonds between D- and C-atoms.

[b] Experimental values of long range deuterium isotope effects (LRDIE/ppb) on C–13 chemical shifts.

[c] Isotope effects not resolved due to line broadening and C–D coupling.

basis is 0.968 for the X-ray geometry (full line) and 0.954 for the 6-31G fully optimized geometry (dashed line).

One can see (Table I) that five- and seven-bond isotope effects are deshielding while six- and ten-bond deuterium isotope effects are shielding effects. Eight- and nine-bond deuterium isotope effects were not experimentally detected. For the nine-bond effect, the line is sharp and we were confident that in this case the effect does not exist. Negligible charge differences calculated at C–3' and C–5' are in agreement with this observation. An eight-bond effect at C–2',6' may exist since the line is

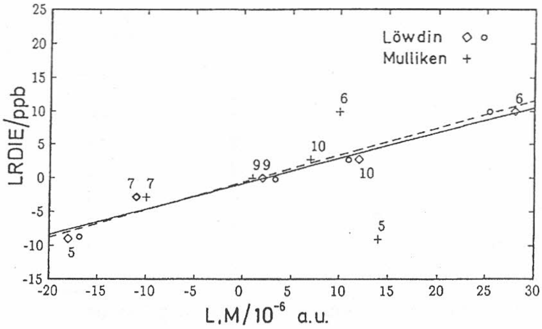

Figure 2. Correlation between LRDIE and the differences of Mulliken and Löwdin charges in 4-D-tSB for C-atoms five, six, seven, nine, and ten bonds away from the deuterium calculated at 6-31G level. For Mulliken charges, no correlation exists, r^2 = 0.006. For Löwdin charges, from the X-ray geometry r^2 = 0.968 (full line) while from fully optimized geometry r^2 = 0.954 (dashed line).

broad. However, it cannot be experimentally resolved due to the overlapping of signals of the protonated and deuterated species and because of the additional signal broadening of C–2,6 in the deuterated molecule caused by the three-bond C–D coupling. The charge difference, which is several times greater for the eight-bond effect than for the nine-bond effect, is in accord with the signal broadening for the former.

A number of empirical and semi-empirical charge-shift relationships have been established for aromatic molecules.[14,24,25] The one of Hehre *et al.*[25] gives the chemical shift change of 384 ppm/electron for substituted benzenes using STO-3G while that of Fliszar *et al.*[14] predicts 300 ppm/electron for aromatic molecules of different ring size using INDO on the GIAO basis. Application of our model to 4-D-tSB molecule gives the charge-shift value of 378.5 ppm/electron using the X-ray geometry and the value of 405 ppm/electron using fully optimized geometry (Figure 2). On this basis we estimated that the eight-bond effect might range from 2.6 ppb (fully optimized geometry) to 2.8 ppb (X-ray geometry).

To the best of our knowledge, there are no experimental data on CCH/CCD bond angle differences although this is conceivable for deuterium substitution at unsymmetrical sites. Some authors explained large intrinsic deuterium isotope effects on C–13 chemical shifts in rigid saturated molecules by changes of bending modes on deuteration.[26] In symmetric molecules like 4-D-tSB no difference between average CCD and CCH bond angles is expected. However, in order to mimic the hypothetical deuterium effect on bending vibrations in 4-D-tSB, we reduced the corresponding CCH in-plane and out-of-plane bending angles by 1.3° and 2°, respectively, in agreement with the theoretical predictions (see computational methods).[23]

TABLE II.

Löwdin charge differences (in 10^{-6} a.u.) calculated for the C–H bond shortening and out-of-plane and in-plane CCH bending angle changes in 4-deutero-*trans*-stilbene using the 6-31G basis set and X-ray geometry.

Atom	N[a]	C–H redb	CCH OOP[c]	CCH IPd	LRDIE[e]
α	5	–18	12	–22	–9
α'	6	28	–24	29	10
1'	7	–11	7	–4	–2.8
2'	8	7	–4	1	0[f]
6'	8	8	–5	3	0[f]
3'	9	2	1	–1	0
5'	9	2	0	–2	0
4'	10	12	–7	1	2.8

[a] Number of intervening bonds between D- and C-atoms.

[b] C–H bonds reduction of 0.012 Å (no bond angle changes).

[c] out-of-plane CCH bending angle change of 2°.

[d] in-plane CCH bending angle change of 1.3°.

[e] Experimental long range deuterium isotope effects (in ppb) on C–13 chemical shift.

[f] Isotope effect not resolved due to line broadening and C–D coupling.

The effects of CCH bending angle changes on Löwdin charge differences are shown in Table II. The hypothetical out-of-plane CCH bending angle change of 2° gives rise to charge differences throughout the molecule. However, calculated charge changes are of opposite sign to the experimentally measured LRDIE and to charge changes calculated with the C–H bond reduction. The charge changes due to the hypothetical in-plane CCH bending angle reduction have a shorter range than the corresponding changes due to out-of-plane angle reduction. From Table II one can see that in-plane CCH bending angle change influences charges negligibly in the second benzene ring cf tSB.

In order to analyze the dependence of the Löwdin charge differences on the molecular dihedral angle in tSB (where this angle is the one between the benzene ring and ethylenic group), we performed calculations with dihedral angles of 6°, 20°, 45° and 90° (Table III). Benzene rings were rotated in the same direction, *i.e.* in-phase, corresponding to the C_i symmetry. The value of 6° is the X-ray angle while 22° value corresponds to the 6-31G fully optimized geometry of tSB.[18] Even in the case of the 90° angle, the C–H bond reduction produces differences of charges throughout the molecule, though of lower magnitude than for the smaller dihedral angles. This is in accord with the experimental observation of longrange deuterium isotope effects in some unconjugated molecules[18,27] and in molecules with conjugated bonds but large dihedral angles,[27,28] giving supportive evidence for the π-polarization effect of deuterium in aromatic molecules.[28] It has been assumed that the π-polarization mechanism consists of two parts: direct- and extended-π-polarization. The extended polarization depends on the molecular dihedral angle and disappears for 90°, while the direct polarization is independent of the dihedral angle and remains even for large dihedral angles.[28] There are also some other reports that the magnitude and extent of long range deuterium isotope effects depend on the molecular dihedral angle and that the π-polarization by deuterium plays a role there.[29,30]

TABLE III.

Dependence of Löwdin charge differences (in 10^{-6} a.u.) on the molecular dihedral angle[a] od 4-deutero-*trans*-stilbene calculated with 6-31G basis sets using X-ray geometry.

Atom	N[b]	6°	22°	45°	90°	LRDIE[c]
α	5	–18	–20	–25	–26	–9
α'	6	28	28	28	29	10
1'	7	–11	–10	–10	–10	–2.8
2'	8	7	6	5	2	0[d]
6'	8	8	7	5	2	0[d]
3'	9	2	2	3	3	0
5'	9	2	2	3	4	0
4'	10	12	11	10	8	2.8

[a] Angle between benzene and ethylene moiety (*e.g.* 2-1-α-α' and 6'-1'-α'-α).

[b] Number of intervening bonds between D- and C-atoms.

[c] Experimental long range deuterium isotope effects (in ppb) on C–13 chemical shifts.

[d] Isotope effect not resolved due to line broadening and C–D coupling.

TABLE IV

Löwdin charge differences (L), empirical (Emp.) isotope shifts, and LRDIE for 4-deutero-BP, -tSB and -cSB with 6-31G fully optimized geometries.

Atom	BP			tSB			cSB		
	L[a]	Emp.[c]	LRDIE[c]	L	Emp.[c]	LRDIE	L	Emp.[c]	LRDIE
α	–	–	–	–17	–6.8	–9	–25	–10	–9.5
α'	–	–	–	25	10	10	30	12	8.6
1'	–14	–5.6	–9.5	–11	–4.4	–2.8	–18	–7.2	–4
2'	1	0.4	0	7	2.8	0[d]	4	1.6	0
6'	1	0.4	0	6	2.4	0[d]	–3	–1.2	0
3'	9	3.6	0[d]	3	1.2	0	4	1.6	0
5'	9	3.6	0[d]	3	1.2	0	6	2.4	0
4'	14	5.6	4.1	11	4.4	2.8	10	4	2

[a] in 10^{-6}a.u.

[b] ppb, calculated from the empirical charge/shift relationship 0.4 ppb/10^{-6}a.u.

[c] ppb, experimental values.

[d] Isotope effects not resolved due to line broadening and C–D coupling.

Table IV shows the correlation between the Löwdin charge differences for 4-D-BP, 4-D-tSB and 4-D-cSB, empirical deuterium isotope shifts, and experimental LRDIE, while Table V presents the same parameters for 4-D-DPA and 4-D-4'-Me-DPB. All molecules were fully optimized at the 6-31G level. In Figure 3, correlation between

TABLE V

Löwdin charge differences (L), empirical isotopes shifts (Emp.), and LRDIE for 4-deutero-DPA and 4-deutero-4'-methyl-DPB[a] with 6-31G fully optimized geometries.

Atom	DPA			DPB		
	L[b]	Emp.[c]	LRDIE[d]	L	Emp.	LRDIE[e]
α	–34	–13.6	–7.2	–22	–8.8	–9
α'	46	18.4	15.6	27	10.8	10
β	–	–	–	16	–6.4	0
β'	–	–	–	26	10.4	7
1'	–13	–5.2	–3.1	–8	–3.2	0
2'	6	2.4	0	6	2.4	0
6'	6	2.4	0	5	2.0	0
3'	2	0.8	0	0	0	0
5'	1	0.4	0	1	0.4	0
4'	9	3.6	2.7	9	3.6	2

[a] the molecule without methyl group was also calculated but no experimental data are available for comparison.

[b] in 10^{-6}a.u.

[c] ppb, calculated from the empirical charge/shift relationship 0.4 ppb/10^{-6} a.u.

[d] ppb, experimental values.

[e] ppb, experimental values from literature.[16]

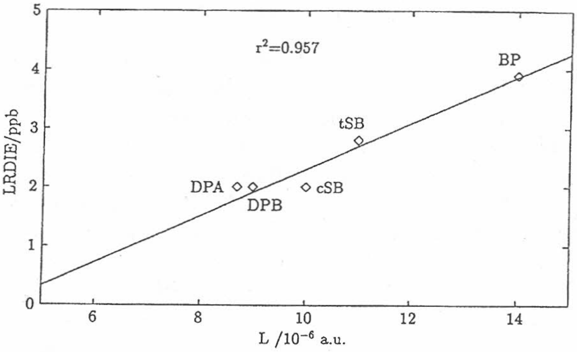

Figure 3. Correlation between the longest LRDIE in 4-D-biphenyl (BP), 4-D-*trans*-stilbene (tSB), 4-D-*cis*-stilbene (cSB), 4-D-diphenylacetylene (DPA), and 4-D-4'-Me-diphenylbutadiene (DPB) and the corresponding Löwdin charge difference calculated for 6-31G fully optimized geometries.

the longest LRDIE in 4-D-BP (8 bonds), 4-D-tSB (10 bonds), 4-D-cSB (10 bonds), 4-D-DPA (10 bonds) and 4-D-4'-Me-DPB (12 bonds) and the corresponding Löwdin charge difference is displayed. The r^2 of 0.957 for fully optimized geometries was established giving a 394 ppm/electron value. In Tables IV and V, empirical shifts were calculated by using the mean charge/shift value of both of our correlations, which amounts to *ca.* 400 ppm/electron. This is only a 4% higher value than the one of Hehre *et al.*,[24] which amounts to 384 ppm/electron. The latter was obtained for compounds containing one substituted benzene ring while our value refers to deuterated molecules containing two linked benzene rings, which might be the cause of the observed difference.

For the first time, our calculations correctly reproduce the signs and magnitude changes of experimantal LRDIE (previous calculations[12] could reproduce only effects up to two bonds). One can see that the majority of the calculated LRDIE displayed in Tables IV and V are within 2–3 times the digital resolution (0.67 ppb), which determines the range of uncertainty of the measurements. Some higher values may arise from vibrational contributions which were not recognized in vibrational analysis. As seen from Tables IV and V, the calculated values of the longest LRDIE are systematically greater than the experimental values, which might also indicate that the mean C–H bond reduction of 0.012 Å estimated from different spectroscopic measurements is too big (as we have found that the charge change is a linear function of bond reduction for small displacements, felt even as far as ten bonds away). For instance, the longest LRDIE experimentally found is over twelve bonds in 4-D-4'-Me-DPB, amounting to 2.0 ppb, while the value obtained from our calculations is 3.6 ppb (the difference is twice our experimental digital resolution). Empirical isotope shifts calculated using the Fliszar *et al.* value of 0.3 ppb/10^{-6} a.u. (derived for a large number of aromatic molecules of different ring size) are even in better agreement with our experimental data.[14] Using the charge difference from our calculations and the Fliszar *et al.* empirical values, one obtains a twelve-bond effect of 2.7 ppb, which is much closer to the experimental 2.0 ppb value. In this respect, better agreement between experimental and calculated isotope effects might be possible if a larger data set of experimental LRDIE in a variety of molecules were available.

CONCLUSION

The *ab initio* calculations showed that the subtle reduction of the C–H bond length or out-of-plane CCH bending angle, which simulates deuterium substitution, gives rise to charge changes throughout the π-molecules. However, good correlation was found only between the LRDIE and Löwdin charge changes, which, together with the lack of vibrational coupling of C–D stretching with vibrations of C-atoms remote from the site of deuteration, gives supportive evidence for LRDIE predominantly arise from the small difference between the average C–D and C–H bond length at the site of deuteration. This difference induces a charge redistribution in the whole molecule on deuterium substitution, also observed by microwave spectroscopy, which in turn contributes to LRDIE on C–13 NMR chemical shifts. It is known that, in a series of related molecules, the change in total shielding is governed mainly by the local paramagnetic term, which enables correlations of chemical shifts with charges. Since isotopomers are the most closely related molecules, correlation of the experimental LRDIE on C–13 chemical shifts with charge differences is conceivable. Due to the lack of gross electron diffrence between isotopomers, the charge/shift relationship derived from isotopically labelled molecules should be more reliable than the relationships derived for molecules with "real" substituents. The very good correlation of the Löwdin charge differences with LRDIE and poor correlation for Mulliken charge diffrences may be an indication that Löwdin charges are more sensitive to subtle electronic changes. Since X-ray geometries are easily accessible from CSDS[22] (giving only 10% greater values of charge differences than fully optimized geometries, which is in agreement with somewhat lower dihedral angles from the X-ray), calculation of the Löwdin charge differences may be used as a simple and fast method for probing experimental LRDIE on C–13 NMR chemical shifts. The results reported here corroborate the concept of the contribution of polarization of the C–C–π bond to the total C–13 chemical shift value.[31]

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SAŽETAK

Modeliranje deuterijskih izotopnih pomaka dugoga dosega u ^{13}C–NMR spektrima binuklearnih aromatskih molekula s pomoću Löwdinovih atomskih naboja

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Deuterijski izotopni efekti dugoga dosega na kemijske pomake u spektrima ^{13}C–NMR proračunani su *ab initio* računima, kao razlike atomskih naboja u nedeuteriranim i deuteriranim molekulama, rabeći pri tom bazne skupove STO-3G, 6-31G, 6-31G** i MIDI. Ukupni atomski naboji izračunani su za bifenil, *trans*-stilben, *cis*-stilben, difenilacetilen, 4'-Me-difenilbutadien i njihove 4-D-derivate. Mjesto deuteracije (C–D veza) simulirano je skraćenjem odgovarajuće veze C–H za 0.012 Å ili smanjenjem odgovarajućeg kuta ravninskog savijanja CCH za 1,3° ili izvanravninskog savijanja za 2°. Računi su provedeni na temelju geometrije kristalnog stanja i geometrije dobivene potpunom optimalizacijom baznim skupom 6-31G. Razlike naboja dobivene s pomoću Mullikenove populacijske analize pokazale su izostanak korelacje (za 6-31G r^2 = 0.006) ili slabu korelaciju (za MIDI r^2 = 0.77) s ekeperimentalno izmjerenim deuterijskim izotopnim efektima (LRDIE) na ^{13}C kemijske pomake. Razlike naboja dobivene s pomoću Löwdinove populacijske analize s 6-31G, 6-31G** i MIDI vrlo dobro koreliraju s eksperimentalno izmjerenim izotopnim efektima na C–13 kemijske pomake C-atoma udaljenih 5, 6, 7, 8, 10 i 12 veza od mjesta deuteriranja. Korelacija vrijedi samo za skraćenje veze, a ne i za promjenu kuta savijanja veze što ukazuje na dominaciju vibracijskih modova istezanja veze nad modovima savijanja veze u doprinosu izotopnom efektu. Mullikenova populacijska analiza pokazala je nezadovoljavajuću korelaciju s eksperimentalnim rezultatima. Analizom vibracija (6-31G) nije utvrđena sprega istezanja C–D veze s vibracijama udaljenih C-atoma, pa se pretpostavlja da izračunana preraspodjela naboja nastala deuteriranjem molekule, opažena također i u mikrovalnim spektrima deuteriranih molekula, uzrokuje deuterijske efekte dugoga dosega na ^{13}C kemijske pomake. To je u skladu s nedavno predloženim doprinosom π-polarizacije C–C veze ukupnoj vrijednosti C–13 kemijskog pomaka.