CROATICA CHEMICA ACTA CCACAA **58** (1) 5—14 (1985)

YU ISSN 0011-1643
CCA-1552 UDC 541.1
Original Scientific Paper

Crystallographic Studies and Physico-Chemical Properties of π-Electron Compounds. Part II. Crystal and Molecular Structure of 2,4-Dinitrobenzoic Acid (DNBA)

Tadeusz Wieckowski and Tadeusz M. Krygowski*

Department of Chemistry, University of Warsaw, 02093 Warsaw, ul. Pasteura 1, Poland

Received August 17, 1983

The crystal structure of the title compound has been determined by single-crystal X-ray diffraction studies from 1043 reflections. The crystals are monoclinic with $a = 6.2150(7)$ Å $b = 14.393(2)$ Å, and $c = 9.487(1)$ Å, $\beta = 97.175(9)^\circ$, space group $P2_1/c$, and $Z = 4$. The structure was solved by direct methods and refined by full-matrix least-squares to a final $R = 0.050$.

The molecule are paired by hydrogen bonding between the carboxy-groups (O—H ... O 2.656(3) Å), the two halves of the dimer being related by a centre of symmetry. It was found that the planes of the two carboxy-groups in the dimer are separated by a distance 0.113 Å.

The significant difference between α_{COOH} values for para substituted benzoic acids with σ-electron withdrawing and -releasing substituents, 1.4(1)°, was found.

The Lippincott-Schroeder model[28] was applied to describe the properties of the H-bridge in DNBA and six other, accurately determined, crystal structures of para-substituted benzoic acids.

The amplitudes of internal motion of the substituents are estimated in terms of the Dunitz and White model.[33]

INTRODUCTION

Carboxylic acids are well known as convenient systems to study substituent effects[1] as well as to analyze the structure and properties of an H-bridge.[2,3] Recently it has been found[4] that the O···O distance in the H-bridge of *p*-substituted benzoic acids, which measures approximately the strength of H-bond, does not follow the Hammett rule. On the other hand, it is known that the internal angle at substituted carbon of the benzene ring varies roughly in a linear way with σ_I or electronegativity of the substituent (the Domenicano rule).[5,6] This discrepancy between substituent effects on structural properties of exo-and endocyclic parameters of substituted benzenes was interpreted[4] in terms of packing forces which influence strongly exocyclic subsituents of the system, overcoming more subtle intramolecular substituent effects. Hence, carboxylic acids are often intensively studied in order to test theories of the H-bridge[7,8] as well as to analyze packing forces.[9]

---

* Present address: Division of Chemistry, National Research Council, Ottawa K1A OR9, Canada.

Considering the known structures of p- and o-nitrobenzoic acids[10,11,12] it was interesting to study DNBA in order to analyze the role played by the second NO_2 group in DNBA in comparison with the mononitro derivatives.

EXPERIMENTAL

Commercial DNBA (Fluka A. G.) was used. The crystals were obtained with two different shapes. Applying the diffusing crystallization technique with acetone as the diffusing solvent and benzene as the original solvent, the crystals grown were plates with $\{110\}$, $\{010\}$ and $\{012\}$ forms. By slow cooling a methanolic solution of DNBA, the crystals grown were prisms with $\{010\}$, $\{110\}$ and $\{001\}$ forms. The latter, which have a much more convenient shape for diffractometric measurements, were chosen for further studies.

Crystallographic measurements

Oscillation and Weissenberg photographs showed the crystal to be monoclinic. A pale yellow prismatic crystal of dimensions $0.23 \times 0.30 \times 0.40$ mm was used for intensity collection. The intensities were measured on a Syntex $P2_1$ four-circle computer-controlled diffractometer with CuKα radiation monochromated by graphite up to $2\Theta = 115.0°$ The cell constants were determined by the least-squares treatment of 15 reflexions with 2Θ values between 12.3 and 34.1°.

Crystal data (at 20 °C) are: $C_7H_4N_2O_6$, M = 212.12. Monoclinic, $a = 6.2150(7)$, $b = 14.393(2)$, $c = 9.487(1)$ Å, $\beta = 97.175(9)°$, $V = 842$ Å^3, $D_m = 1.67$ g cm^{-3} (flotation in aqueous KI), $Z = 4$, $D_c = 1.670$ g cm^{-3} m. p.: 181—182 °C, $F(000) = 432$. CuKα radiation ($\lambda = 1.54178$ Å), μ (CuKα) = 13.4 cm^{-1}. Systematic absences $0k0$ with $k = 2n + 1$ and $h0l$ with $l = 2n + 1$ uniquely define the space group as $P2_1/c$.

The $\Theta — 2\Theta$ scan technique was employed at a scan rate varying from 2.01 to 29.30° min^{-1} in 2Θ.

The intensities were measured for 1130 unique reflexions, of which 1043 were classified as observed. A reflexion was considered as unobserved if $I_{obs} < 1.960\,\sigma(I)$, where $\sigma(I)$ was calculated from the counting statistics. Lorentz and polarization factors were applied but no correction was made for absorption or extinction.

Structure Solution and Refinement

The crystal structure was solved by the direct multisolution method with the MULTAN program[13] using 133 E's ≥ 1.50 for which 893 Σ_2 relationships were generated.

A six-cycles refinement of the non-hydrogen atom coordinates by full-matrix least-squares procedures with individual isotropic thermal parameters unit weights gave R = 0.168; the CRYLSQ program in the XRAY 70 system[14] was used with minimization of $\Sigma w\,(|F_o| — |F_c|)^2$. Subsequently, the quantities $1/\sigma^2\,(F_o)$, where $\sigma\,(F_o)$ was as defined by Stout and Jensen,[15] were used to weigh the least-squares differences for the observed data.

The vibrational model was then changed to an anisotropic one and five subsequent cycles of least-squares refinement were attempted; R was reduced to 0.080. The next six cycles of refinement, with H-ring atom positions calculated geometrically by using the XANADU program[16] resulted in $R = 0.052$ and $R_w = 0.067$.

A difference Fourier map revealed distinctly the position of the carboxylic H-atom. Finally, the coordinates and isotropic temperature factors of the H-atom in the carboxylic group were refined in six additional cycles of refinement. The analysis was based on scattering factors for neutral atoms taken from International Tables for X-ray Crystallography.[17] Refinement converged with R = 0.050 and $R_w = \{\Sigma w\Delta^2/\Sigma wF_o^2\} = 0.059$.

The average shift/error value at the end of the refinement procedure was 0.003. The computations were performed on a CDC 6600 (CYBER-72) computer.

The final fractional coordinates from the last cycle of the least-squares refinement of non-hydrogen atoms (including the H-atom involved in an H-bond) are given in Table I*.

TABLE I

Fractional Coordinates (× 10^4) for Non-hydrogen Atoms (Including, However, the H *Atom (×* 10^3*) Involved in an* H*-bond). Estimated Standard Deviations from the Final Full-matrix Least-squares Cycle are Given in Parentheses*

Atom	*x*	*y*	*z*
C1	7543(5)	2958(2)	646(3)
C2	8203(5)	2059(2)	386(3)
C3	7208(5)	1283(2)	856(3)
C4	5453(5)	1436(2)	1581(3)
C5	4690(5)	2306(2)	1850(4)
C6	5753(5)	3070(2)	1370(4)
C7	8684(5)	3830(2)	282(3)
O1	10564(4)	3945(1)	994(3)
O2	7767(4)	4397(1)	—553(2)
N1	9998(4)	1906(2)	—474(3)
O3	10886(4)	1156(2)	—411(3)
O4	10471(5)	2549(2)	—1203(3)
N2	4318(5)	619(2)	2061(3)
O5	4943(5)	—143(2)	1738(3)
O6	2849(5)	747(2)	2770(4)
HO1	1124(5)	454(2)	79(4)

RESULTS

The atom-labelling scheme and the anisotropic thermal ellipsoids of the DNBA molecule are shown in Figure 1. Bond lengths and angles are shown in Figure 2. The shortest intermolecular distances (less than 3.4 Å) are listed in

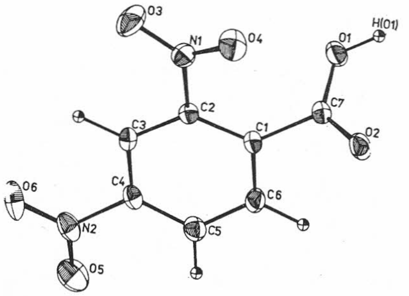


Figure 1. Thermal ellipsoid plot (ORTEP, Johnson[35]) showing vibration ellipsoids at the 50% probability level.

---

* Thermal parameters (Table II), positions of hydrogen atoms (Table III) and comparison of observed and calculated structure factors are available on request.

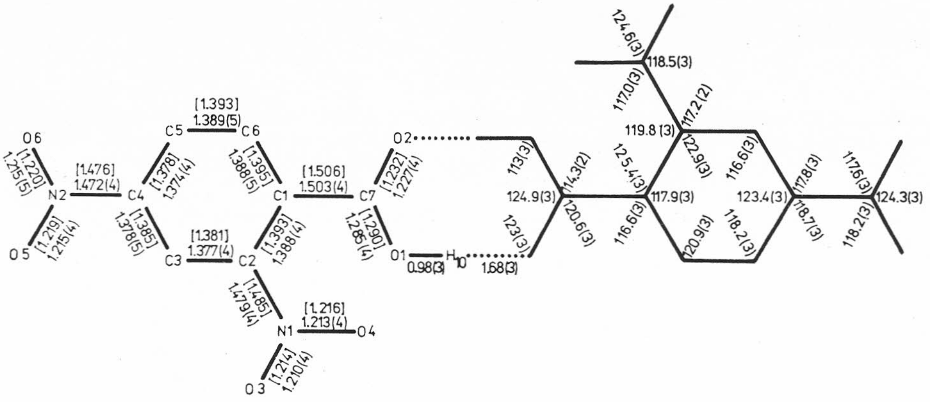


Figure 2. The number scheme for the atoms together with bond lengths (Å) and angles (°). The bond lengths in the upper line are corrected for libration.

Table IV. Table V gives the least-squares planes for the atoms Cl through C6, (plane 1), C1, C7, O1, O2 (plane 2), C2, N1, O3, O4 (plane 3) and C4, N2, O5, O6 (plane 4). The angles between the above-mentioned planes are listed in Table VI.# Figure 3 represents a projection of the unit cell along the {001} direction.

TABLE IV

Intermolecular Contacts ⟨ 3.4 Å Involving Non-hydrogen Atoms in DNBA Crystal

$O_2 \ldots C_4^{(i)}$	3.149(4) Å	$O_5 \ldots C_6^{(v)}$	3.196(4) Å
$O_2 \ldots C_7^{(ii)}$	3.362(4)	$O_5 \ldots O_2^{(vi)}$	3.116(3)
$O_2 \ldots N_2^{(i)}$	2.917(4)	$O_6 \ldots O_2^{(vi)}$	3.271(4)
$O_3 \ldots C_4^{(iii)}$	3.233(4)	$O_6 \ldots O_3^{(vii)}$	3.166(4)
$O_3 \ldots N_2^{(iii)}$	3.065(4)	$O_6 \ldots O_4^{(viii)}$	3.083(4)
$O_5 \ldots C_3^{(iv)}$	3.117(4)		

Estimated standard deviations calculated from the variance-covariance matrix obtained in the final least-squares cycle are given in parentheses.

Roman numerals as superscripts refer to the following equivalent positions, relative to the reference molecule at x, y, z:

(*i*)	$x, \frac{1}{2} - y, -\frac{1}{2} + z$	(*v*)	$1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$
(*ii*)	$2 - x, 1 - y, -z$	(*vi*)	$x, \frac{1}{2} - y, \frac{1}{2} + z$
(*iii*)	$1 + x, y, z$	(*vii*)	$-1 + x, y, z$
(*iv*)	$1 - x, -y, -z$	(*viii*)	$-1 + x, \frac{1}{2} - y, \frac{1}{2} + z$

Table V and Table VI are available on request.

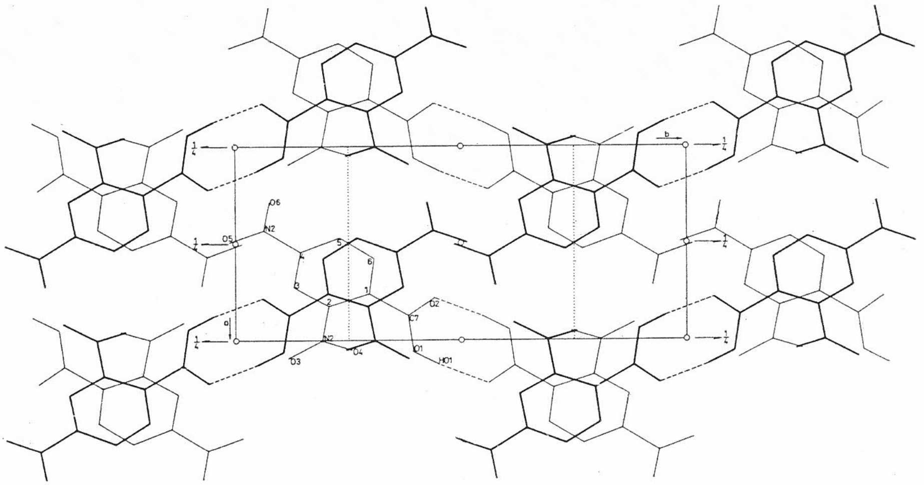


Figure 3. View of the crystal structure down c.

DISCUSSION

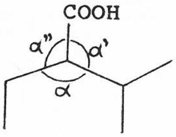
(i) Geometry of the Ring

Two parameters, valence angles and bond lengths, describe the geometry of the benzene ring. It is usually considered[18] that both are affected by substituents. Following the Walsh rule[19] the C—C bonds adjacent to the substituted carbon atom are shortened when the substituent is electron withdrawing. In the DNBA-molecule all substituents are of this character and the shortening of CC-bond lengths in the ring is expected. In fact C_2C_3-, C_3C_4- and C_4C_5-bonds are considerably shorter than the others, as shown clearly in Figure 2. In consequence the mean bond length for ring bonds is $\overline{R} = 1.387$ Å, whereas for benzene $\overline{R} = 1.392$ Å, for the X-ray measurements corrected for libration.[20]

Both nitro groups influence the endocyclic angle at substituted carbon atoms in nearly the same way yielding $\alpha = 123.4°$ and $122.9°$; these values are in good agreement with other data for the nitro group: $\alpha = 123.7°$ for o-nitrobenzoic acid[12] and $\alpha = 123.3°$ [10] and $\alpha = 122.6°$ [11] for *p*-nitrobenzoic acid.

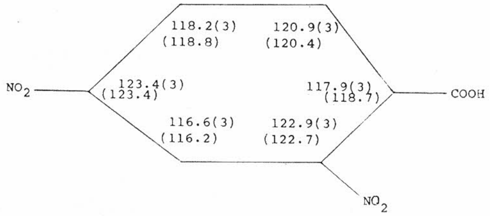
Following Domenicano *et al.*[18] the valence angle at the carbon atom substituted by COOH should be about 120° for unsubstituted and *para*-substituted benzoic acids. In the DNBA molecule $\alpha_{\mathrm{COOH}} = 117.9°$. Similar values are observed for: o-nitrobenzoic acid[12] with α (at COOH) $= 116.2°$, o-N,N-dimethylaminobenzoic acid[21] and o-aminobenzoic acid [22] for which $\alpha = 117.0°$ and $118.0°$. Our finding and those mentioned above may be partially explained in terms of intramolecular interactions between non-bonded atoms in the o-substituent and the carboxyl group. In most of those systems the closest contacts between the interacting atoms of *ortho*-substituents are lower or much lower than the sum of the Van der Waals radii. In the case of DNBA the closest contacts are $R\,(O_4 \cdots O_1) = 2.891$ Å and $R\,(O_4 \cdots C_7) = 2.648$ Å whereas the sums of Van der Waals radii for these contacts are 3.04 Å and 3.22 Å[24] respectively.

Due to the interactions described above, the X substituent repels the COOH group yielding a larger α'-angle. As a consequence the sp^2-hybridization at the C-atom is perturbed, leading in turn to a decrease of two other angles α and α'':



Hence α becomes lower as a result of steric hindrance of the *ortho*-substituent.

This effect is apparent while applying the additivity rule of substituent effect on the ring geometry. Applying the most recent angular parameters[25] for NO_2 and COOH the results obtained are given on the scheme below (calculated data in parentheses):



Only calculated value for α_{COOH} differs distinctly from its experimental value. This result supports our suggestion on mechanism of interactions for *o*-substituents.

Another problem arises when looking at α_{COOH} for *para*-substituted benzoic acids. According to Domenicano *et al.*[18] the mean value of the internal angle $\overline{\alpha}_{COOH}$ at the ipso carbon of the ring is 119.8° for five *para*-substituted benzoic acids. Colapietro *et al.*[26,27] have studied the molecular geometries of several *para*-substituted benzoic acids. Their comparison has shown small structural effect of the *para*-substituent on the α_{COOH} angle. Actually the geometries of almost 20 molecules of *para*-substituted benzoic acids are available. More detailed analysis of the problem leads to the result that $\overline{\alpha}_{COOH}$ for *para*-substituted benzoic acids with σ-electron-withdrawing substituents equals to $120.2(1)^\circ$ whereas for σ-electron-releasing substituted acids $\overline{\alpha}_{COOH} = 118.8(1)^\circ$. The difference is significant and indicates the importance of intramolecular interactions between the COOH-group and the *para*-substituent. Hence it should be stated that a substituent in *para*-position does influence the α_{COOH} and this effect depends on the electronic properties of the substituent.

(ii) Geometry of Substituents

The geometry of the substituents may be discussed in terms of their bond lengths and valence angles as well as of dihedral angles between the planes of the substituents and that of the benzene ring. Within experimental error the NO_2 groups in DNBA possess axial symmetry in agreement with the data for *p*-nitrobenzoic acid,[10] but in opposition to the geometry of the NO_2 group in *o*-nitrobenzoic acid[12] where the geometry deviates considerably from axial symmetry. As seen in Table IV, the intermolecular contacts between oxygen atoms in NO_2 groups with other atoms are almost equal to or longer than the sum of the Van der Waals radii and hence axial symmetry of both NO_2 groups is found, as expected. The only slightly shorter contact between O and C is 3.196(4) Å in comparison with the sum of Van der Waals radii of these atoms, 3.22 Å.[24] This interaction is not reflected in a change of the N—O bond length, but only in the r.m.s. thermal motion amplitude of the oxygen atom. Another consequence of both overcrowded *o*-substituents is the considerable displacement of C_7 and N_1 atoms, by 0.126 Å and —0.099 Å, respectively, measured relatively to the plane of the ring. For *o*-nitrobenzoic acid the first figure is 0.209 Å[12] whereas for *p*-nitrobenzoic acid it is —0.019 Å.[10]

The latter finding means almost coplanarity of the ring- and carboxy group-planes in *p*-nitrobenzoic acid.

The intra- and intermolecular interactions are the reason for mutual orientations of planes of the ring and of all substituents. The relevant data are collected in Table VI.

(iii) Application of the Lippincott-Schroeder Model to DNBA and Several p-Substituted Benzoic Acids

The geometry of the hydrogen bond determined by X-ray diffraction analysis can be applied in estimations of such properties as the energy, force constants for OH and $OH\cdots O$ vibrations as well as charge density at oxygen atoms. This has been accomplished for DNBA and several *p*-substituted benzoic acids within the semiempirical model of the hydrogen bond introduced by Lippincott and Schroeder.[28,29]

The results of the analysis are presented in Table VII. Columns 2—4 show the geometry of the H-bridge. Column 5 contains the energies, V_{exp}, of the H-bridge: these values tend to increase with a decrease of the $O\cdots O$ distance.

Column 6 contains the charge-density values at oxygen atoms whereas columns 7—8 present the force constants $k_{O\cdots O}$ and k_{O-H}. Column 9 lists the calculated frequencies of OH vibration (ν_{OH}) involved in the H-bridge.

Apart from the information contained in Table VIII, it is worth mentioning that COOH groups in the dimer of DNBA are parallel, but they do not lie in the same plane. The perpendicular distance between the planes is 0.113 Å. This finding was also observed by Jeffrey[30] for many carboxylic systems and it was interpreted in terms of intermolecular forces.

(iv) Torsional Motions of Substituents

When analyzing the values of atomic root-mean-square amplitudes of vibration of the atoms in the *p*-NO_2 group along the principal axes of the thermal ellipsoids, one can observe a significant difference between the r.m.s. amplitudes of vibration of both oxygen atoms. This appears to be due to the difference in the intermolecular contact for the two atoms. One of them $O_5\cdots C_6^{(v)}$ is equal to 3.196 Å, and is shorter than the sum of Van der Waals radii 3.22 Å.[24] For O_5 $(\langle u^2 \rangle)^{1/2} = 0.22$ Å compared with the value 0.29 Å for O which is not surrounded by such close contacts. For the *ortho*-NO_2 group

TABLE VII

Structure Data ($R_{O...O}$, r_{O-H} and O—H . . . O) for DNBA and Several p-*Substituted Benzoic Acids and Results of the Lippincott-Schroeder Model Calculations*

Acid	O . . . O (Å)	O—H (Å)	O—H . . . O (°)	V_{exp} $\frac{\text{kcal}}{\text{mol}}$	Charge (e^-)	k_{O-H}	$k_{O...O}$	ν_{OH} (cm^{-1})
						($10^5 \times$ dyna. cm^{-1})		
p-Nitrobenzoic[10]	2.660(2)	1.04(2)	177(2)	—8.85	0.251	0.876	4.232	2714.4
(A) *p*-n-Butoxybenzoic[36]	2.600(3)	1.08[L]	179	—10.35	0.288	1.586	2.959	2269.8
(B) *p*-n-Butoxybenzoic[36]	2.652(3)	0.98[L]	166	—7.34	0.222	0.561	6.126	3264.6
p-Fluorobenzoic[37]	2.618(2)	1.11(4)	176(3)	—7.87	0.292	1.676	2.146	1928.9
p-Methoxybenzoic[38]	2.632(2)	1.00(4)	172(3)	—8.90	0.241	0.774	5.421	3068.7
Cinnamic[39]	2.630	1.01	175	—9.35	0.249	0.866	5.075	2971.3
β-(*p*-chlorophenyl) propionic[40]	2.645(3)	0.93(4)	177(3)	—5.35	0.210	0.456	7.227	3548.3
DNBA	2.656(3)	0.98(3)	174(3)	—7.71	0.227	0.600	6.023	3237.8

L — thermally corrected values are based on a riding model.

there are no shorter contacts than the sum of Van der Waals radii, and the r.m.s. thermal motion amplitudes for both oxygens in this group are axially symmetric within experimental error: $(< u^2 >)^{1/2} = 0.25$ and 0.27 Å.

More detailed analysis of the thermal motion of the substituents was carried out by the use of Huber-Buser[31] THMB computer program based upon the theory of Dunitz and White.[32] This theory allows the analysis of thermal motions of the substituents treated as internally rigid, librating usually around the bond relative to the rigid moiety of the ring. An agreement between the calculated and experimentally determined anisotropic temperature factors was tested by using the reliability factor[33] $R_{wU} = [\Sigma w_{ij} (\Delta U_{ij})^2/\Sigma w_{ij} (U_{ij}^{obs.})^2]^{1/2}$ where U_{ij} is the contravariant component of mean square atomic motion tensor (in Å^2) whereas $w_{ij} = (\sigma_{ij})^{-2}$ with σ_{ij} being standard deviation of U_{ij}. A hypothesis for improving the agreement between the calculated anisotropic temperature factors for the non-rigid body model and those determined experimentally for the rigid body model was verified by the Hamilton R-ratio test.[34] The value of R_G/R_{wU} is 1.209 with the number of degrees of freedom 72. Hence, the difference between R_G and R_{wU} is significant at the level of 0.05.

The r.m.s. thermal motion amplitude has the lowest value for the COOH group, 4.9°; due to overcrowding as well as to the H-bond effect in dimers of the two NO_2 groups in the DNBA molecule the *ortho*-group exhibits a smaller value of r.m.s. group libration amplitude, 8.2°, in comparison with more sterically free *p*-group for which it equals to 9.7°. The R_{wU} for DNBA is 0.115, $\Delta U_{ij} = 0.0053$ and $(\sigma_{ij})_{av} = 0.0046$. In comparison, for the COOH group in *p*-nitrobenzoic acid,[11] which is involved in H-bonding but is not sterically hindered the r.m.s. value is as large as 9°.

Acknowledgements. — This study was supported by the Chemical Sciences Committee of the Polish Academy of Sciences.

REFERENCES

1. L. P. Hammet, *Physical Organic Chemistry,* McGraw-Hill, New York, 1970.
2. A. Novak, *Hydrogen Bonding in Solids,* in *Structure and Bonding,* **18** (1974) 177.
3. P. Schuster, G. Zundel, and C. Sandorfy, *The Hydrogen Bond. Recent Developments is Theory and Experiments.* North Holland Publ. Co., Amsterdam, 1976.
4. T. M. Krygowski and T. Wieckowski, *Croat. Chem. Acta* **54** (1981) 193.
5. A. Domenicano, P. Mazzeo, and A. Vaciago, *Tetr. Letters* (1976) 1029.
6. A. Domenicano and P. Murray-Rust, *Tetr. Letters* (1979) 2283.
7. J. L. Derissen and P. H. Smit, *Acta Cryst.* **A34** (1978) 842.
8. A. T. Hagler, P. Dauber, and S. Lifson, *J. Amer. Chem. Soc.* **101** (1979) 5131.
9. L. Leiserowitz, *Acta Cryst.* **B32** (1976) 775.
10. M. Colapietro and A. Domenicano, *Acta Cryst.* **B33** (1977) 2240.
11. S. S. Tavale and L. M. Pant, *Acta Cryst.* **B27** (1974) 1479.
12. S. S. Tavale and L. M. Pant, *Acta Cryst.* **B29** (1973) 2979.
13. G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.* **A27** (1971) 368.
14. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, *The X-Ray System,* Computer Science Center, Univ. of Maryland, College Park, Maryland, 1970.
15. G. H. Stout and L. H. Jensen, *X-Ray Structure Determination.* The Macmillan Company Collier-Macmillan Limited, London, 1968, p. 457.
16. P. J. Roberts and G. M. Sheldrick, Program XANADU, Univ. of Cambridge, England, 1975.

17. *International Tables for X-Ray Crystallography.* Vol. IV. p. 72, Birmingham: Kynock Press, 1974.
18. A. Domenicano, A. Vaciago, and C. A. Coulson, *Acta Cryst.* **B31** (1975) 221.
19. A. D. Walsh, *Discuss. Faraday Soc.* **2** (1974) 18.
20. E. G. Cox, *Rev. Mod. Phys.* **30** (1958) 159.
21. N. N. Dhaneshwar and L. M. Pant, *Acta Cryst.* **B29** (1973) 2980.
22. C. D. G. Boone, J. L. Derissen, and J. C. Schoone, *Acta Cryst.* **B33** (1977) 3205.
23. J. Krausse and H. Dunken, *Acta Cryst.* **20** (1966) 67.
24. A. Bondi, *J. Phys. Chem.* **68** (1964) 441.
25. A. Domenicano, private communication, 1982.
26. M. Colapietro, A. Domenicano, and G. P. Ceccarini, *Acta Cryst.* **B35** (1979) 980.
27. M. Colapietro, A. Domenicano, and G. Portalone, *Acta Cryst.* **B36** (1980) 354.
28. E. R. Lippincott and R. Schroeder, *J. Chem. Phys.* **23** (1955) 1099.
29. R. Schroeder and E. R. Lippincott, *J. Chem. Phys.* **61** (1975) 921.
30. G. A. Jeffrey and M. Sax, *Acta Cryst.* **16** (1963) 430.
31. E. Huber-Buser, unpublished computer program THMB, Organic Chem. Lab. Swiss Federal Institute of Technology, Zyrich, 1977.
32. J. D. Dunitz and D. N. J. White, *Acta Cryst.* **A29** (1973) 93.
33. K. N. Trueblood, *Acta Cryst.* **A34** (1978) 950.
34. W. C. Hamilton, *Acta Cryst.* **18** (1965) 502.
35. C. K. Johnson, ORTEP, Report ORNL — 3794. Oak Ridge National Laboratory, Tennessee, 1965.
36. R. F. Bryan and L. Fallon, *J. Chem. Soc. Perk. II* (1975) 1175.
37. M. Colapietro, A. Domenicano, and G. P. Ceccarini, *Acta Cryst.* **B35** (1979) 980.
38. M. Colapietro and A. Domenicano, *Acta Cryst.* **B34** (1978) 3277.
39. R. F. Bryan and D. P. Freyberg, *J. Chem. Soc. Perk. II* (1975) 1835.
40. J. P. Glusker, D. E. Zacharias, and H. L. Carrell, *J. Chem. Soc. Perk. II* (1975) 68.

SAŽETAK

Kristalografsko istraživanje i fizičko-kemijska svojstva π-elektronskih spojeva. Kristalna i molekulska struktura 2,4-dinitrobenzojeve kiseline (DNBA)

T. Wieckowski i T. M. Krygowski

Kristalna struktura 2,4-dinitrobenzojeve kiseline (DNBA) određena je metodom difrakcije rendgenskih zraka na monokristalu sa 1043 refleksa. Kristali su monoklinski, $a = 6{,}2150(7)$, $b = 14{,}393(2)$ i $c = 9{,}487(1)$ Å, $\beta = 97{,}175(9)^\circ$, prostorna grupa $P2_1/c$ i $Z = 4$. Struktura je riješena direktnim metodama i utočnjena metodom najmanjih kvadrata do konačnog $R = 0{,}050$.

Molekule su spojene u parove preko centrosimetričnih vodikovih veza među karboksilnim grupama (O—H...O 2,656(3) Å). Nađeno je da je razmak među ravninama karboksilnih skupina u dimeru 0,113 Å. Nađena je značajna razlika (1,4(1)°) među vrijednostima α_{COOH} za *para*-supstituiranu benzojevu kiselinu sa supstituentima koji privlače i onima koji oslobađaju σ-elektrone.

Za opis svojstava vodikovog mosta u DNBA i šest drugih, točno određenih, kristalnih struktura *para*-supstituirane benzojeve kiseline primijenjen je Lippincott-Schroederov model.

Amplitude internog gibanja supstituenata analizirane su upotrebom modela Dunitza i Whitea.