

2-Carboxybenzenediazonium Chloride Monohydrate

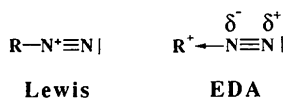
BY CHRISTOPHER J. HORAN,* CHARLES L. BARNES† AND RAINER GLASER‡

Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211, USA

(Received 18 February 1992; accepted 14 September 1992)

Abstract. $C_7H_5N_2O_2^+ \cdot Cl^- \cdot H_2O$, $M_r = 202.60$, monoclinic, $C2/c$, $a = 25.62$ (3), $b = 4.964$ (2), $c = 14.900$ (14) Å, $\beta = 107.15$ (4)°, $V = 1811$ (3) Å³, $Z = 8$, $D_x = 1.486$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71073$ Å, $\mu = 3.9$ cm⁻¹, $F(000) = 832$, $T = 298$ K, $R = 0.035$ for 1275 observed reflections. The terminal N atom of the diazonium group is bent away from the carboxyl group. The N₂ and the carboxyl group are on opposite sides of the best plane of the aromatic ring and, importantly, the carboxyl group is not fully conjugated with the aromatic ring but instead is rotated [12.3 (1)°] around the C—CO₂ axis.

Introduction. We have been studying the 'incipient nucleophilic attack' in diazonium ions as a probe for the electronic structures of diazonium ions (Glaser, Horan, Nelson & Hall, 1992) with theoretical methods and we have proposed a new bonding model based on topological electron density analysis (EDA). In contrast to the Lewis structure which formally implies that the N₂ function carries the positive charge, in our bonding model diazonium ions are best described as carbenium ions associated with an N₂ group that is internally polarized in the fashion $R-N^{\delta-}-N^{\delta+}$ (Glaser, 1989). The crystal structure of the title compound was determined as part of a project to provide experimental data to test further the new theoretically derived bonding model.



Experimental. Crystals were grown by slow cooling of aqueous HCl solution, pH ≈ 2.0. A pale-yellow prism of dimensions 0.30 × 0.35 × 0.40 mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with ω -2 θ scans and Mo $K\alpha$ radiation. 25 reflections with $10 \leq \theta \leq 13^\circ$ were used to refine cell dimensions. Systematic absences: hkl , $h + k = 2n + 1$, $00l$, $l = 2n + 1$. No absorption correction was

applied. Data were collected to $2\theta_{\max} = 50^\circ$ for $-30 \leq h \leq 28$, $0 \leq k \leq 5$, $0 \leq l \leq 17$. Three standard reflections measured after every 3600 s of X-ray exposure indicated less than 2% decay. Of a total of 1621 reflections, 1586 were unique ($R_{\text{int}} = 0.016$) with 1275 observed [$I \leq 2.5\sigma(I)$]. The structure was solved by direct methods. Refinement (on F) minimized $\sum w(F_o - F_c)^2$, with $w = 1/[\sigma^2(F) + 0.0015(F^2)]$. H atoms were located in difference maps and refined with fixed isotropic thermal parameters; non-H atoms were refined with anisotropic thermal parameters. Final refinement with 139 parameters converged at $R = 0.035$, $wR = 0.056$, $S = 1.23$; $(\Delta/\sigma)_{\max} = 3.2\%$; final difference map maximum 0.33, minimum -0.18 e Å⁻³. Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Structure solution and all calculations were performed with *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989).

Discussion. A perspective *ORTEPII* (Johnson, 1976) drawing of the cation with the numbering scheme is given in Fig. 1. Final positional parameters are given in Table 1,† and bond lengths, angles and selected torsional angles are given in Table 2. A *PLUTO* (Motherwell, 1976) molecular packing diagram is given in Fig. 2.

The terminal N atom is displaced away from the carboxyl group resulting in a 6.7 (3)° deviation of the C(2)—N(1)—N(2) skeleton from linearity. This bending is consistent either with attraction of the proximate carbonyl O atom [$O(1) = O_{\text{pr}}$] and a positively charged N(1) ion — as suggested by the *formal* charge in the usual Lewis structure — or with quadrupolar neighboring interactions between $N(1)^{\delta-}$ — $N(2)^{\delta+}$ and the polar carbonyl group as suggested by our recent electron-density analysis of diazonium ions (Glaser, 1989, 1990; Glaser, Choy & Hall,

* Part of the projected PhD dissertation of CJH. Presented in part at the 26th ACS Midwest Regional Meeting, Omaha, Nebraska, November 7, 1991.

† To whom correspondence should be addressed.

‡ Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55675 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR1003]

1991; Glaser, Horan, Nelson & Hall, 1992; Glaser, Horan, Choy & Harris, 1992). The latter views the close approach of O_{pr} to N(1) as a consequence of optimizing C(2),N(2)-1,3-bridging and despite N(1)⋯O_{pr} repulsion, and it is not only consistent with but also provides a simple explanation for the observation that the N₂ and COOH groups are on opposite sides of the best plane of the phenyl ring [dihedral angle N1—C2—C1—C7 = 7.4 (1)^o]. This displacement increases the N(1)⋯O_{pr} distance and thus seems inconsistent with the assumption of N(1)⋯O_{pr} attraction.

The Cl ion located on the twofold axis, Cl(1), is solely involved in two hydrogen bonds [Cl(1)⋯O(2) 2.948 (3) Å] with the acidic H atoms of two neighboring monomers. The Cl ion located on the inversion center, Cl(2), is positioned between two monomers in a C(2),N(2)-1,3-bridging fashion between both diazonium functionalities. Again, we refer to this side-on coordination of the Cl ion to the CNN function as 1,3-bridging because the electronic structure analysis suggests attractive interaction of the Cl ion with C(2) and N(2) but not with N(1). Note that the shorter distance between Cl and N(1) compared to its distance to C(2) does not contradict the argument (Glaser & Streitwieser, 1987). In addition, these Cl ions are hydrogen bonded

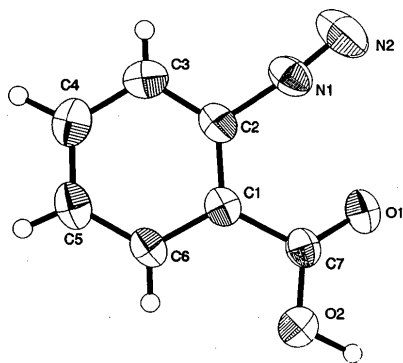


Fig. 1. Perspective view of the cation with numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Note the conformation of the carboxyl group is such that the carbonyl O atom is oriented toward the diazonium group.

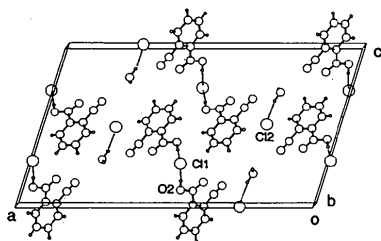


Fig. 2. View of the packing interactions down the *b* axis.

Table 1. Positional and equivalent isotropic thermal parameters (Å²)

B_{eq} is the mean of the principal axes of the thermal ellipsoid (Hamilton, 1959).

	x	y	z	B_{eq}
C(1)	0.09164 (8)	0.5612 (4)	0.48012 (13)	2.87 (8)
C(2)	0.13229 (8)	0.3700 (4)	0.48425 (14)	3.07 (8)
C(3)	0.15190 (10)	0.1907 (5)	0.55657 (18)	3.78 (10)
C(4)	0.12999 (10)	0.2006 (5)	0.63026 (16)	4.05 (10)
C(5)	0.08923 (9)	0.3840 (5)	0.62933 (15)	3.84 (10)
C(6)	0.07028 (9)	0.5625 (5)	0.55481 (14)	3.26 (9)
C(7)	0.07535 (8)	0.7597 (4)	0.40136 (13)	2.97 (8)
O(1)	0.10229 (7)	0.7910 (3)	0.34792 (11)	3.81 (7)
O(2)	0.03150 (6)	0.8965 (3)	0.40095 (11)	4.02 (7)
N(1)	0.15373 (8)	0.3432 (4)	0.40801 (14)	3.70 (8)
N(2)	0.17213 (11)	0.2997 (5)	0.35269 (18)	5.71 (13)
Cl(1)	0	1.30181 (17)	↓	4.31 (4)
Cl(2)	↓	↓	↓	4.03 (4)
O(W)	0.76135 (11)	0.2690 (4)	0.29565 (15)	5.92 (12)

Table 2. Bond lengths (Å), bond angles (°) and selected torsion angles (°)

C(1)—C(2)	1.397 (3)	C(4)—C(5)	1.383 (4)
C(1)—C(6)	1.378 (3)	C(5)—C(6)	1.391 (3)
C(1)—C(7)	1.494 (3)	C(7)—O(1)	1.208 (3)
C(2)—C(3)	1.374 (3)	C(7)—O(2)	1.311 (3)
C(2)—N(1)	1.406 (3)	N(1)—N(2)	1.085 (3)
C(3)—C(4)	1.373 (4)		
C(2)—C(1)—C(6)	115.87 (19)	C(3)—C(4)—C(5)	120.07 (23)
C(2)—C(1)—C(7)	120.98 (17)	C(4)—C(5)—C(6)	120.82 (21)
C(6)—C(1)—C(7)	123.07 (20)	C(1)—C(6)—C(5)	120.88 (22)
C(1)—C(2)—C(3)	124.78 (19)	C(1)—C(7)—O(1)	121.40 (20)
C(1)—C(2)—N(1)	119.49 (19)	C(1)—C(7)—O(2)	112.69 (17)
C(3)—C(2)—N(1)	115.64 (21)	O(1)—C(7)—O(2)	125.85 (20)
C(2)—C(3)—C(4)	117.57 (23)	C(2)—N(1)—N(2)	173.3 (3)
C(6)—C(1)—C(2)—C(3)	-0.6 (1)	C(6)—C(1)—C(2)—N(1)	175.8 (2)
C(7)—C(1)—C(2)—C(3)	176.1 (2)	C(7)—C(1)—C(2)—N(1)	-7.4 (1)
C(2)—C(1)—C(6)—C(5)	0.7 (1)	C(7)—C(1)—C(6)—C(5)	-176.0 (2)
C(2)—C(1)—C(7)—O(1)	-12.3 (1)	C(2)—C(1)—C(7)—O(2)	170.5 (2)
C(6)—C(1)—C(7)—O(1)	164.2 (2)	C(6)—C(1)—C(7)—O(2)	-13.0 (1)
C(1)—C(2)—C(3)—C(4)	-0.1 (1)	N(1)—C(2)—C(3)—C(4)	-176.7 (3)
C(1)—C(2)—N(1)—N(2)	-163.3 (3)	C(3)—C(2)—N(1)—N(2)	13.4 (2)
C(2)—C(3)—C(4)—C(5)	0.8 (1)	C(3)—C(4)—C(5)—C(6)	-0.7 (1)
C(4)—C(5)—C(6)—C(1)	0.0 (1)		

[Cl(2)⋯O(W) 3.144 (3) Å] with lattice water. The water O atom is located along the CNN vector at a distance of 3.168 (3) Å from N(2).

In the structure of 3-carboxy-2-naphthalenediazonium chloride (Gougoutas & Johnson, 1978), the two functional groups are on opposite sides of the naphthalene plane and the CNN skeleton also deviates from linearity in the discussed fashion, but these structural characteristics were interpreted with the N(1)⋯O_{pr} attraction model. Interestingly, and in contrast to the naphthalene system, the carboxyl group is rotated around the C—CO₂ axis [C(2)—C(1)—C(7)—O(1) = 12.3 (1)^o] in the benzene derivative in such a way that the N(1)⋯O_{pr} distance is increased. The rotation of the carboxyl group might be a further manifestation of N(1)⋯O_{pr} repulsion but it is equally consistent with the optimization of the hydrogen bonds of the carboxyl groups with the Cl ions. Note that the structure of the naphthalene analogue is nearly planar and has no such hydrogen bonds.

Other articles discussing distortions related to the incipient nucleophilic attack of proximate nucleophiles on diazonium functionalities include reports by Gougoutas (1979, 1982), Wallis & Dunitz (1984) and Greenberg & Okaya (1969).

Acknowledgement is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, and the MU Research Council (92-RC-023-BR), for support of this research. The X-ray diffractometer was partially funded by the National Science Foundation (CHE 90-11804).

References

- GABE, E. J., LE PAGE, Y., CHARLAND, J.-P., LEE, F. L. & WHITE, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- GLASER, R. (1989). *J. Phys. Chem.* **93**, 7993–8003.
- GLASER, R. (1990). *J. Comput. Chem.* **11**, 663–679.
- GLASER, R., CHOY, G. S.-C. & HALL, M. K. (1991). *J. Am. Chem. Soc.* **113**, 1109–1120.
- GLASER, R., HORAN, C. J., CHOY, G. S.-C. & HARRIS, B. (1992). *Phosphorus Sulfur Silicon*. In the press.
- GLASER, R., HORAN, C. J., NELSON, E. & HALL, M. K. (1992). *J. Org. Chem.* **57**, 215–228.
- GLASER, R. & STREITWIESER, A. (1987). *J. Am. Chem. Soc.* **109**, 1258–1260.
- GOUGOUTAS, J. Z. (1979). *J. Am. Chem. Soc.* **101**, 5672–5675.
- GOUGOUTAS, J. Z. (1982). *Cryst. Struct. Commun.* **11**, 1305–1310.
- GOUGOUTAS, J. Z. & JOHNSON, J. (1978). *J. Am. Chem. Soc.* **100**, 5816–5820.
- GREENBERG, B. & OKAYA, Y. (1969). *Acta Cryst.* **B25**, 2101–2108.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- JOHNSON, C. K. (1976). *ORTEP II*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting crystal and molecular structures. Univ. of Cambridge, England.
- WALLIS, J. D. & DUNITZ, J. D. (1984). *J. Chem. Soc. Chem. Commun.* pp. 671–672.

Acta Cryst. (1993). **C49**, 509–511

Structure of an Organic Photochromic Compound. 6,7,8a,9-Tetrahydro-17,17-dimethylnaphtho[1'',2'':5',6'] [1,4]oxazino[3',2':2,3] [1,4]oxazino[4,3-a] [3H]indole

BY ANDREW TEH HU* AND MING-SING WANG

Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan 300

AND SUE-LEIN WANG

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300

(Received 28 April 1992; accepted 29 July 1992)

Abstract. Following the general procedure for the synthesis of spirooxazines, an unexpected new compound was obtained: $C_{23}H_{22}N_2O_2$, $M_r = 358.4$, monoclinic, $P2_1/n$, $a = 13.215$ (3), $b = 9.321$ (1), $c = 15.600$ (4) Å, $\beta = 105.68$ (2)°, $V = 1850.0$ (7) Å³, $Z = 4$, $D_x = 1.287$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.077$ mm⁻¹, $F(000) = 760$, $T = 296$ K, final $R = 0.0389$, $wR = 0.0415$ for 1775 reflections with $I \geq 3.0\sigma(I)$. This new compound, in chloroform solution, shows a colour change on irradiation with UV light or exposure to sunlight, and reverts to a light brown colour when kept in the dark after the removal of UV light.

Introduction. Organic photochromic compounds have attracted significant attention in view of their potential applications in optical memory devices, light filters, optical switches, actinometers, dec-

oration, *etc.* (Bertelson, 1971; Guglielmetti, Chu, Gauglitz, Ichimura, Michl, Wild, Renn, Hampp & Brauchle, 1990). Spirooxazines are important photochromic compounds because of their good fatigue resistance to light.

The chemical structure of the spirooxazine (I) (Millini, Del Piero, Allegrini, Crisci & Malatesta, 1991) is very similar to that of the spiropyran (II) (Kellmann, Tfibel, Dubest, Levoir, Aubard, Pottier & Guglielmetti, 1989), a photochromic compound of current interest. The only difference between (I) and (II) is that (I) has a C=N bond in place of the C=C bond in (II). On exposure to UV light, both undergo a colour change and the C(spiro)—O bond is cleaved heterolytically. The reverse colour change occurs when the irradiated form is exposed to visible light or heat.

In general, spirooxazines are directly synthesized by the reaction of an indoleninium salt with an *ortho*-nitroso aromatic alcohol (Nakamura & Tani-

* To whom correspondence should be addressed.