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Symmetrically H-Bridged Dimer of 2-Carboxylatobenzenediazonium. The 1:1 Complex Between 2-Carboxybenzenediazonium Chloride and Benzenediazonium-2-carboxylate

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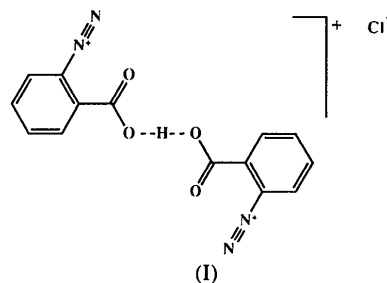
Abstract

The two zwitterions in the H-bridged dimer of 2-carboxylatobenzenediazonium (1) are linked by a crystallographically symmetric O \cdots H \cdots O hydrogen bond with an O \cdots O distance of 2.436 (3) Å. Comparison of (1) with other benzenediazonium salts shows that the phenyl ring distortions in (1) are determined primarily by the diazonium substituent with only modest additional effects by the carboxylate group. Intramolecular neighboring group

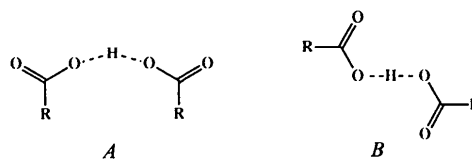
interactions between the N₂ group and the *ortho* COO(H) group are indicated and are discussed. The terminal N atom of the diazonium group is bent away from the neighboring carboxylate group. The N₂ and the carboxylate group are on *opposite* sides of the best plane of the aromatic ring. Importantly, the carboxylate group is not fully conjugated with the aromatic ring but instead is rotated 6.5 (2)° around the C—CO₂ axis in a fashion that suggests minimization of *intramolecular* repulsion between N _{α} and the proximate O atom and optimization of the *intermolecular* hydrogen bonding.

Comment

The crystal structure of the H-bridged dimer of the 2-carboxylatobenzenediazonium system, (1), was determined as part of our studies of the incipient nucleophilic attack in diazonium ions. These studies of the incipient nucleophilic attack serve as a probe for the electronic structures of diazonium ions (Glaser, Horan, Nelson & Hall, 1992) which we have been studying with *ab initio* methods.



The crystal structure is characterized by aggregates of two 2-carboxylatobenzenediazonium zwitterions, (1). An H atom, located on a center of symmetry, hydrogen bonds between the carboxylate O atoms of two neighboring zwitterions. In general, unsymmetrical hydrogen bonds between two O atoms lead to O \cdots O distances within the range 2.6–2.7 Å, while symmetrical hydrogen bonds have shorter O \cdots O distances of about 2.5 Å (Cupertino, Harding, Cole-Hamilton, Dawes & Hursthouse, 1986). In (1), the observed intermolecular distance O(2) \cdots O(2) of 2.436 (3) Å is thus consistent with a *symmetric* hydrogen bond. While there have been several reports of intramolecular hydrogen bonding between proximate carboxylate groups of the type *A* (e.g. Hsu



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& Schlemper, 1978, 1980; Küppers, 1978), the structural motif *B* has been observed much less frequently. Aside from (1), type *B* intermolecular symmetric hydrogen bonding has been described by Howard-Lock, Lock, Martins, Faggiani & Duarte (1987), by Cupertino *et al.* (1986) and by Misaki, Kashino & Haisa (1989).

Benzene substituents are well known to alter primarily the C—C—C angle at the *ipso* C atom with smaller and counteracting angle changes at the adjacent C atoms (Domenicano, 1992). The resulting characteristic distortions of the phenyl ring in (1) are caused primarily by the diazonium substituent, with only modest additional effects by the carboxylate group. The angle at the *ipso* C atom of the diazonium function is C(1)—C(2)—C(3) = 125.7 (3)°, and the adjacent angles, C(6)—C(1)—C(2) = 114.9 (3)° and C(2)—C(3)—C(4) = 116.8 (3)°, are slightly smaller than 120°. Importantly, these distortions are qualitatively the same as those found in the phenyl cation and they indicate substantial positive charge on the phenyl ring of the diazonium ions. In the phenyl cation, the C—C—C angle at the electron-deficient C atom is greatly increased to about 145° (Dill *et al.*, 1976) in order for the C⁺ to increase its *s* character. The phenyl ring in (1) is distorted in a very similar fashion; this motif also occurs in simple benzenediazonium salts of the type PhN₂⁺X⁻, including the chloride, (2) (Rømming, 1963), the tribromide, (3) (Andresen & Rømming, 1962) and the tetrafluoroborate, (4) (Cygler, Przybylska & Eloffson, 1982). In (1) to (4), the C(1)—C(3) distance increases (2.437–2.492 Å) as the angle at C(2) increases (124.8–131°), distorting the phenyl ring from *D*_{6h} symmetry. The C(2)—N(1) bond in (1) [1.415 (4) Å] is longer than in (2) [1.385 (9) Å], but equal in length to that observed in (3) [1.41 (5) Å] and in (4) [1.415 (3) Å]. The N≡N triple-bond length of 1.076 (4) Å also corresponds to that found in (2), (3) and (4) [1.083 (3)–1.11 (5) Å].

Each Cl ion assumes a 1,3-bridging position with regard to the C—N≡N group. C(2) is at a distance of 3.666 (3) Å from the Cl ion, the terminal N atom N(2) is at a distance of 3.300 (3) Å, and the inner N atom N(1) is at a distance of 3.217 (3) Å. Our recent topological studies of the electronic structures of related diazonium ions (Glaser, 1989, 1990; Glaser, Choy & Hall, 1991; Glaser *et al.*, 1992) revealed charge distributions of the type C(2)⁺—^{δ-}N(1)—N(2)^{δ+} which are fully consistent with such 1,3-bridging. Similar distances with the counterion are observed in (2) to (4) and in all of these salts four anions surround each diazonium function and, in each case, the distances between the counterion and N(2) and N(1), respectively, are not too different. These results on PhN₂⁺X⁻ suggested a significant positive charge on the terminal N atom which is also

consistent with the results of our electron-density analysis.

In the H-bridged dimer (1), the terminal N atom, N(2), is displaced away from the carboxyl group resulting in a 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_{pr}) and a positively charged N(1) (as suggested by the commonly used Lewis structure) or with *quadrupolar* neighboring interactions between ^{δ-}N(1)—N(2)^{δ+} and the intramolecular polar carbonyl group. Our interpretation views the close approach of a proximate nucleophile (O_{pr}) to N(1) as a *consequence* of optimizing the attractive interactions between O_{pr} and the positive termini of the C(2)—N(1)≡N(2) fragment and occurs *despite* N(1)—O_{pr} *repulsion*. The invocation of N(1)—O_{pr} repulsion 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 = 7.0 (2)°]. This displacement increases the N(1)—O_{pr} distance and thus seems inconsistent with the assumption of N(1)—O_{pr} attraction. In a similar situation, the structure of 3-carboxy-2-naphthalenediazonium chloride, (5) (Gougoutas & Johnson, 1978) shows both of these structural characteristics but was interpreted with the simple electrostatic N(1)—O_{pr} attraction model. A significant difference occurs between (1) and (5) which has important consequences for the discussion of neighboring group interactions. In the crystal structure of (5), the carboxyl group is essentially coplanar with the phenyl ring. Importantly, in (1) the carboxyl group is rotated around the C—CO₂

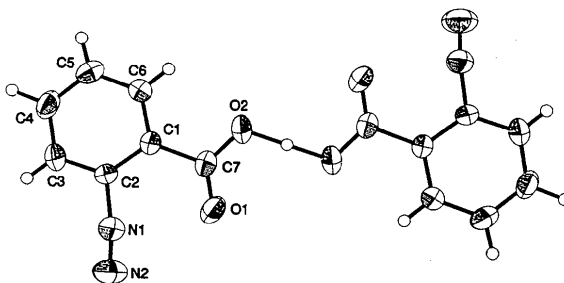


Fig. 1. Perspective view (ORTEP; Johnson, 1976) of the molecule with numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

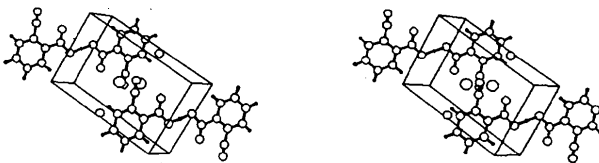


Fig. 2. Stereoview (PLUTO; Motherwell, 1976) of the packing interactions.

axis [C2—C1—C7—O1 = 6.5 (2)°] in such a fashion 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 bonding of the carboxylate groups with one another. Furthermore, the carboxyl rotation might also reflect hydrogen bonding between the carbonyl O atom and the lattice water since these O atoms are 2.686 Å apart, which is a typical distance for non-symmetrical hydrogen bonding.

References concerning distortions related to the incipient nucleophilic attack of proximate nucleophiles with diazonium functionalities include reports by Gougoutas (1979, 1982), Wallis & Dunitz (1984), and Greenberg & Okaya (1969) and reports by us on the structures of the closely related hydrates of 2-carboxylatobenzenediazonium zwitterion (Horan, Barnes & Glaser, 1993b) and of 2-carboxybenzenediazonium chloride (Horan *et al.*, 1993a).

Experimental

Crystal data

C₇H₄N₂O₂·C₇H₅N₂O₂⁺·Cl⁻·
2H₂O

M_r = 184.37

Triclinic

*P*1̄

a = 4.8238 (15) Å

b = 7.510 (2) Å

c = 11.915 (4) Å

α = 84.37 (2)°

β = 80.74 (2)°

γ = 78.18 (2)°

V = 416.03 (22) Å³

Z = 1

D_x = 1.472 Mg m⁻³

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25
reflections

θ = 10–15°

μ = 0.41 mm⁻¹

T = 298 K

Prism

0.44 × 0.22 × 0.20 mm

Pale yellow

Crystal source: slow cooling
of acidic (pH = 4) aque-
ous solution

Data collection

Enraf–Nonius CAD-4
diffractometer

ω–2θ scans

Absorption correction:
none

1647 measured reflections

1459 independent reflections

1117 observed reflections
[*I* ≤ 2.5σ(*I*)]

*R*_{int} = 0.016

θ_{max} = 25°

h = –5 → 5

k = 0 → 8

l = –13 → 14

3 standard reflections

frequency: 60 min

intensity variation: <2.5%

Refinement

Refinement on *F*²

Final *R* = 0.058

wR = 0.075

S = 1.84

1117 reflections

127 parameters

Only coordinates of H atoms
refined

w = 1/[σ²(*F*) + 0.0015(*F*²)]

(Δ/σ)_{max} = 0.043

Δρ_{max} = 0.44 e Å⁻³

Δρ_{min} = –0.33 e Å⁻³

Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

H atoms were located in a difference map and refined with fixed isotropic thermal parameters; it was not possible to locate the H atoms of the water molecules, apparently because of their disordered positions. Computations employed the *NRCVAX* program package (Gabe, Le Page, Charland, Lee & White, 1989).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

*B*_{eq} is defined as the mean of the principal axes of the thermal ellipsoid (Hamilton, 1959).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
C(1)	0.1492 (6)	0.3282 (4)	0.84367 (24)	2.83 (11)
C(2)	0.3532 (6)	0.3700 (4)	0.75438 (23)	2.82 (11)
C(3)	0.5929 (7)	0.2499 (4)	0.7086 (3)	3.64 (13)
C(4)	0.6319 (7)	0.0736 (4)	0.7569 (3)	3.98 (14)
C(5)	0.4407 (8)	0.0252 (5)	0.8470 (3)	4.17 (15)
C(6)	0.2029 (7)	0.1507 (4)	0.8902 (3)	3.80 (13)
C(7)	–0.1167 (7)	0.4603 (4)	0.8838 (3)	3.19 (12)
O(1)	–0.1716 (5)	0.6074 (3)	0.82992 (21)	4.52 (11)
O(2)	–0.2712 (5)	0.4005 (3)	0.97136 (19)	4.25 (10)
N(1)	0.3278 (6)	0.5513 (4)	0.70583 (23)	3.70 (12)
N(2)	0.3370 (8)	0.6845 (5)	0.6646 (3)	5.80 (18)
Cl(1)	0	0.5	0.5	4.45 (5)
H(O)	–0.5	0.5	1.0	4.74 (20)
O(W)	0.2129 (7)	0.0759 (4)	0.0759 (4)	6.44 (16)

Table 2. Bond lengths (Å), bond angles (°), selected torsion angles (°) and plane with atomic deviations (Å)

C(1)—C(2)	1.387 (4)	C(4)—C(5)	1.371 (5)
C(1)—C(6)	1.383 (4)	C(5)—C(6)	1.389 (5)
C(1)—C(7)	1.494 (4)	C(7)—O(1)	1.224 (4)
C(2)—C(3)	1.384 (4)	C(7)—O(2)	1.280 (4)
C(2)—N(1)	1.415 (4)	N(1)—N(2)	1.076 (4)
C(3)—C(4)	1.379 (5)		
C(2)—C(1)—C(6)	114.9 (3)	C(3)—C(4)—C(5)	120.1 (3)
C(2)—C(1)—C(7)	123.3 (3)	C(4)—C(5)—C(6)	121.1 (3)
C(6)—C(1)—C(7)	121.8 (3)	C(1)—C(6)—C(5)	121.4 (3)
C(1)—C(2)—C(3)	125.7 (3)	C(1)—C(7)—O(1)	119.0 (3)
C(1)—C(2)—N(1)	119.2 (3)	C(1)—C(7)—O(2)	114.2 (3)
C(3)—C(2)—N(1)	115.0 (3)	O(1)—C(7)—O(2)	126.8 (3)
C(2)—C(3)—C(4)	116.8 (3)	C(2)—N(1)—N(2)	172.7 (3)
C(6)—C(1)—C(2)—C(3)	1.8 (2)	C(6)—C(1)—C(2)—N(1)	–175.9 (4)
C(7)—C(1)—C(2)—C(3)	–175.3 (4)	C(7)—C(1)—C(2)—N(1)	7.0 (2)
C(2)—C(1)—C(6)—C(5)	–1.7 (2)	C(7)—C(1)—C(6)—C(5)	175.4 (5)
C(2)—C(1)—C(7)—O(1)	6.5 (2)	C(2)—C(1)—C(7)—O(2)	–176.2 (4)
C(6)—C(1)—C(7)—O(1)	–170.4 (5)	C(6)—C(1)—C(7)—O(2)	6.9 (2)
C(1)—C(2)—C(3)—C(4)	–0.4 (2)	N(1)—C(2)—C(3)—C(4)	177.3 (5)
C(1)—C(2)—N(1)—N(2)	160.8 (5)	C(3)—C(2)—N(1)—N(2)	–17.1 (3)
C(2)—C(3)—C(4)—C(5)	–1.1 (2)	C(3)—C(4)—C(5)—C(6)	1.1 (2)
C(4)—C(5)—C(6)—C(1)	0.4 (2)		

Equation of the plane

3.392 (5) *x* + 3.320 (10) *y* + 9.128 (11) *z* = 9.306 (6)

Distances to the plane from the atoms in the plane

C1	–0.009 (4)	C2	0.006 (4)
C3	0.003 (4)	C4	–0.010 (4)
C5	0.004 (5)	C6	0.008 (4)

χ² = 18.833

Distances to the plane from the atoms out of the plane

C7	–0.106 (5)	O1	–0.297 (6)
O2	–0.030 (6)	N1	0.079 (5)
N2	0.176 (7)		

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71076 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR1005]

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Structure of Boc-Phe-D-Leu-OMe

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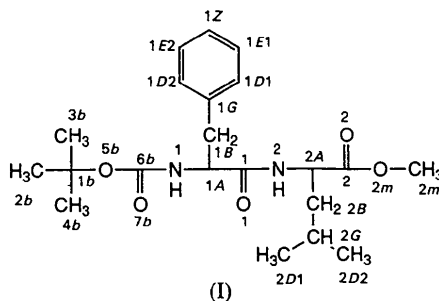
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Abstract

The X-ray crystal structure analysis of *tert*-butoxycarbonyl-L-phenylalanyl-D-leucine methyl ester showed two crystallographically independent molecules, each of them taking a similar open conformation in which the *tert*-butoxycarbonyl group and D-leucine isobutyl side chain are located facing parallel to each other. In the crystal, these molecules are piled up alternately along the *b* axis and form an infinite sheet structure through four independent NH...O—C hydrogen bonds.

Comment

As one of a series of investigations into the relationship between the molecular conformation and the hydrophobicity/hydrophilicity of oligopeptides consisting of L-L, L-D or D-L sequences, the title peptide (I) was chemically synthesized and its molecular conformation determined by X-ray crystal analysis. The conformational study is also interesting in that this sequence constitutes a part of DADLE (H-Tyr-D-Ala-Gly-Phe-D-Leu-OH), an opioid peptide specific for the δ -receptor, and plays an important role in its activity (Zajac, Gacel, Petit, Dodey, Rossignol & Roques, 1983).



The atomic positional and equivalent isotropic thermal parameters are listed in Table 1. Table 2 lists some conformational torsion angles. There are two crystallographically independent molecules per asymmetric unit. Each of them, named molecules *A* and *B*, takes a similar open or extended conformation in