Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.096$
$S = 0.968$
1342 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0786P)^2 + 0.0649P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 0.139$ e Å^{-3}
$\Delta\rho_{\min} = -0.153$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

N—C7	1.377 (4)	C1—C9	1.468 (4)
N—C9	1.401 (4)	C6—C7	1.471 (4)
N—C8	1.452 (4)	C9—C10	1.343 (4)
O1—C7	1.212 (4)	C10—C11	1.475 (4)
O2—C11	1.224 (4)	C11—C12	1.481 (4)
C7—N—C9	112.5 (2)	N—C7—C6	105.7 (2)
C9—N—C8	124.9 (2)	N—C9—C1	105.5 (2)
C6—C1—C9	108.0 (2)	C9—C10—C11	126.3 (3)
C1—C6—C7	108.4 (3)	C10—C11—C12	118.6 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*···*A*	*D*—H···*A*
C10—H10···O2^{i}	3.441 (4)	164.2 (2)
C8—H8*B*···O2^{i}	3.301 (4)	117.9 (2)
C8—H8*C*···O1^{ii}	3.453 (4)	126.4 (2)
C16—H16···O1^{iii}	3.364 (4)	122.6 (2)
C17—H17···O1^{iii}	3.222 (4)	126.5 (2)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{3}{2}-y, -z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (iii) $x, 1+y, z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *MULTAN*88 (Debaerdemaeker *et al.*, 1988). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1995). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1246). Services for accessing these data are described at the back of the journal.

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2*H*-Dibenzo[*b*,*f*]azepin-2-one

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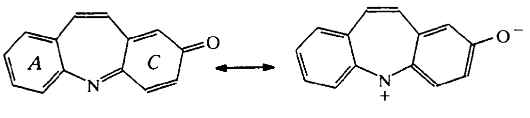
Abstract

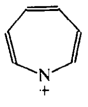
It has been postulated that the title compound, $C_{14}H_9NO$, (1*a*), may play a role in idiosyncratic reactions induced by carbamazepine, one of the most widely used anticonvulsants in North America. Compound (1*a*) was found to be nearly planar, unlike its parent compound iminostilbene. The possibility of the azepinone having a resonance contribution from the novel nitrenium ion was investigated. The slightly elongated C═N and C═O bond lengths suggest that there is some contribution from the nitrenium structure. However, the alternating bond lengths show that the major resonance contributor is the iminoquinone.

Comment

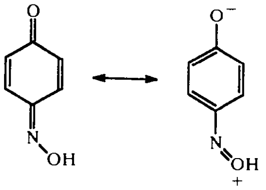
Nitrenium ions, (1*b*), are of considerable biological importance. Reactions proceeding *via* such intermediates have been investigated extensively, especially as models for processes involved in carcinogenesis by aromatic amines (McClelland, 1996). The actual cellular target is often DNA and indeed covalent adducts of guanine residues have been observed *in vivo* (Schut & Castongauy, 1984), as well as in model systems (Underwood *et al.*, 1988). The molecule under investigation in this work, (1*a*), is believed to be an active metabolite associated with the adverse reactions experienced by up to 50% of patients undergoing treatment for convulsive disorders while taking carbamazepine (5*H*-dibenzo[*b*,*f*]-azepine-5-carboxamide). The iminoquinone is an active electrophile and it may bind to macromolecules *in vivo* to cause direct toxicity or act as a hapten to modulate the immune system (Ju & Uetrecht, 1999).



(1*a*) (1*b*)



(2)



(3*a*) (3*b*)

The crystal structure of 2*H*-dibenzo[*b*,*f*]azepin-2-one, (1*a*), was obtained with the express interest of determining the contribution that the novel nitrenium ion, (1*b*), makes to the overall structure. The latter contains a central azepine ring that can be looked upon as the nitrogen analogue of the well known tropylium cation (Kolomnikova & Parnes, 1967; Von Doering & Knox, 1954; Pietra, 1973; Hafner, 1964). All attempts to prepare or detect the parent heterotropylium cation, (2), have to date failed, although intermediacy of a benzoazatropylium ion and azatropylium ions has been suggested for the fragmentation of 1-methylisoquinoline or of various substituted phenylazides (Marx & Djerassi, 1968; Abramovitch, 1961). It is not at all clear why (2) remains unknown since it seems to fit all the necessary prerequisites of aromaticity, assuming the intermediate exists in its singlet state. The lack of an empty *p* orbital in the triplet state would disrupt the ring current and destroy the aromaticity; however, there is no reason to believe that such an intermediate would exist in the triplet state. Our immediate goal herein is to determine whether (1*b*) contributes significantly to the overall structure, and hence to make a judgement on the possibility of *O*-alkylation or *O*-silylation to yield the elusive aromatic nitrenium ion.

From the crystal structure, it is clear that ring *A* possesses a high degree of aromaticity. The bond lengths do vary, but only in the range 1.3750 (19)–1.4177 (18) Å. Ring *C*, on the other hand, shows alternation typical of structure (1*a*), with bond lengths alternating between 1.3361 (19) and 1.4747 (18) Å for double and single bonds, respectively. The molecule is almost planar; it is distorted from planarity by 2.70 (7) and 3.66 (7)° for rings *A* and *C*, respectively, relative to the central azepine ring, so that the dihedral angle between rings *A* and *C* is 6.31 (7)°. In contrast, iminostilbene has a pronounced butterfly structure with a dihedral angle between rings *A* and *C* of 35.6 (1)° (Reboul *et al.*, 1980).

Few data pertaining to the crystal structure of iminoquinones exist in the literature; the closest molecule with this substructure was studied by Talberg (1974). Talberg determined the crystal structure of 4-quinone oxime, (3), and concluded that the bond lengths indicate a considerable degree of π resonance. Both the carbonyl [1.243 (3) Å] and the imine [1.305 (3) Å] bond lengths were found to be longer than typically expected values [1.22 and 1.276 (5) Å, respectively]. The lengthening of both of these bonds indicates a significant aromatic character in the 4-quinone oxime. Interestingly, values of 1.2402 (17) and 1.3040 (16) Å were determined for the carbonyl and imine bond lengths, respectively, in the title compound. Thus, our results parallel those of Talberg, in that both systems have the imine and carbonyl bond lengths elongated slightly (by approximately 0.02 Å) with respect to normal analogues. We therefore conclude that a similar degree of π resonance exists in 2*H*-dibenzo[*b*,*f*]azepin-2-one, (1*a*), that structure (1*b*) does in fact contribute to the overall structure and that there is some degree of aromaticity in ring *C* of the title compound. We caution that the results of Talberg are less accurate than those presented here, but feel that the contribution from the nitrenium ion, (1*b*), is real. However, the alternating bond order in ring *C* indicates that the major resonance contributor is structure (1*a*). The possibility of electrophilic addition to the partially negative O atom leading to the elusive nitrenium ion now exists and will be investigated by us.

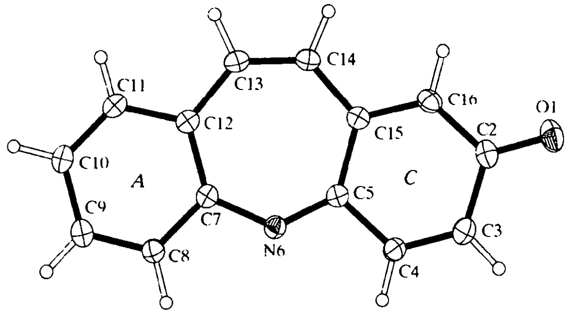


Fig. 1. A view of the title molecule showing the atom-labelling scheme. Ellipsoids are at the 30% probability level.

Experimental

The title compound was synthesized by the oxidation of commercially available iminostilbene, by the action of Fremy's salt; a modification of the method used by Skibo & Islam (1991) was incorporated. The iminoquinone product was recrystallized over a period of one week from hexane.

Crystal data

$C_{14}H_9NO$
$M_r = 207.22$
Monoclinic
$C2/c$
$a = 11.5121\,(3)$ Å
$b = 8.5186\,(3)$ Å
$c = 20.4454\,(7)$ Å
$\beta = 100.768\,(2)°$
$V = 1969.71\,(11)$ Å^3
$Z = 8$
$D_x = 1.398$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 7403 reflections
$\theta = 4.45$–$26.37°$
$\mu = 0.089$ mm^{-1}
$T = 150.0\,(1)$ K
Fragment cut from needle
0.30 × 0.26 × 0.25 mm
Purple

Data collection

Nonius Kappa-CCD diffractometer
1° φ scans
Absorption correction: none
7403 measured reflections
1996 independent reflections
1682 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.049$
$\theta_{\rm max} = 26.37°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 10$
$l = -25 \rightarrow 25$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.099$
$S = 1.035$
1996 reflections
146 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 1.2397P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.190$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.139$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.013 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C2	1.2402 (17)	N6—C7	1.3921 (16)
C2—C16	1.451 (2)	C7—C12	1.4177 (18)
C2—C3	1.456 (2)	C12—C13	1.4427 (18)
C3—C4	1.3361 (19)	C13—C14	1.3450 (19)
C4—C5	1.4585 (18)	C14—C15	1.4420 (19)
C5—N6	1.3040 (16)	C15—C16	1.3616 (18)
C5—C15	1.4747 (18)		
C16—C2—C3	116.20 (12)	C7—C12—C13	125.45 (12)
C4—C3—C2	120.86 (13)	C14—C13—C12	130.32 (13)
C3—C4—C5	123.22 (13)	C13—C14—C15	130.13 (13)
N6—C5—C4	112.60 (11)	C16—C15—C14	117.80 (12)
N6—C5—C15	130.57 (12)	C16—C15—C5	118.57 (12)
C4—C5—C15	116.82 (11)	C14—C15—C5	123.64 (12)
C5—N6—C7	130.74 (11)	C15—C16—C2	124.13 (13)
N6—C7—C12	128.91 (12)		

Data collection: *Kappa-CCD Server Software* (Nonius, 1997). Cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997). Data reduction: *DENZO-SMN*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1517). Services for accessing these data are described at the back of the journal.

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2-Amino-4-phenylthiazole

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Abstract

The title compound, $C_9H_8N_2S$, is almost planar, with an angle of 6.2 (3)° between the planes of the phenyl and thiazole rings. Molecules are linked by an intermolecular