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**Crystal Structure
Communications**

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2-(Phenylaminomethylidene)cyclohexane-1,3-dione

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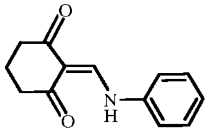
In the title compound, $C_{13}H_{13}NO_2$, there is polarization of π-electron density from the amine N atom to the acceptor carbonyl groups: as a result, the molecule exists predominantly in an azomethino-1,3-diketone tautomeric form. There is crystallographic evidence that the phenyl ring, although roughly coplanar with the rest of the molecule, is deconjugated with the adjacent π system of the molecule. The cyclohexane ring adopts an unsymmetrical half-chair conformation and converts between two inversion-related conformers. The molecule is stabilized by an intramolecular hydrogen bond, while the intermolecular packing is dominated by a number of short C—H···O contacts.

Comment

Recently, as part of our ongoing study on the structure–activity relationships of biologically active compounds, we focused our attention on the title compound, (I), following reports that such derivatives exhibit photobleaching activity as assayed in tobacco (*Nicotiana tabacum*) cultured cells (Wang *et al.*, 1997). It was shown that the chlorophyll and carotenoid contents of cells treated with the cyclic dione disappeared within 24 h under light, but not dark, conditions. However, the rapid onset of photobleaching activity did not result from inhibition of protoporphyrinogen oxidase, indicating that some other mechanism of action might operate, for example, electron transport between the drug molecule and the photosynthetic pigments. Thus, to shed some light on the molecular mechanism of action, we initiated a study of the π-electronic structure of the dione in both ground and photo-activated states by a combination of theoretical and experimental techniques. In this communication, we report on the crystal structure of (I).

The molecular structure, along with the atom-numbering scheme, is shown in Fig. 1. Atoms C5, C6 and O1 are disordered between two positions, denoted by unprimed (major site) and primed (minor site) labels, respectively. The disorder originates from two conformations of the cyclohexane ring, which are related by an inversion of the ring. A calculation of the least-squares planes has shown that the ring is puckered in such a manner that atoms C1, C2, C3 and C4 are coplanar within experimental error [r.m.s. deviation = 0.002 (2) Å], while atoms C5 and C6 are unequally displaced from this plane on opposite sides, with out-of-plane displacements of −0.531 (7) and 0.227 (12) Å, respectively. The corresponding displacements of atoms C5′ and C6′ in the inverted conformation are 0.518 (9) and −0.264 (15) Å, respectively. Thus, the conformation of the two puckered rings can be described, according to Duax *et al.* (1976), as intermediate between half-chair, with a local pseudo-twofold axis along the mid-points of the C2—C3 and C5—C6 (or C5′—C6′) bonds, and sofa, with a local pseudo-mirror along the C2···C5 (or C2···C5′) direction. The Cremer & Pople (1975) puckering parameters are $Q = 0.499$ (6) Å, $\theta = 50.8$ (3)° and $\varphi = -104.0$ (7)° (calculated for the sequence C1–C6); the corresponding parameters for the inverted ring are $Q = 0.525$ (8) Å, $\theta = 128.7$ (2)° and $\varphi = 79.3$ (7)° (sequence C1–C4/C5′/C6′).



(I)

As noted above, the main purpose of this work was to establish the (π) electron distribution within the π-electronic portion of the molecule. Firstly, as shown in Table 1, the C7—N1—C8 valence angle is larger than 120°, *i.e.* the amine N atom is sp^2-hybridized, with the lone-pair electrons available for π-bonding. Secondly, as estimated from the bond-order–bond-length curves proposed by Burke-Laing & Laing (1976), the bond order of the N1—C7 single bond is higher (~1.7) than that of the C2═C7 double bond (~1.5). Furthermore, the C1—C2 and C2—C3 bond distances are significantly shorter than the normal value of 1.487 Å reported for a Csp^2—Csp^2 single bond (Shmueli *et al.*, 1973). These findings, coupled with the lengthening of the two carbonyl bonds with respect to the range normally accepted for a C═O double bond (1.20–1.22 Å), imply that there is extensive π-electron delocalization

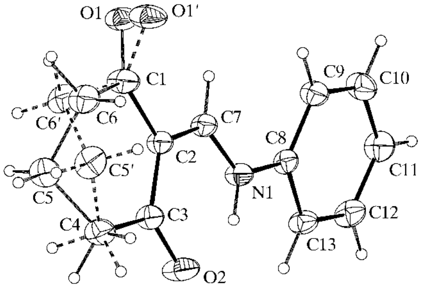


Figure 1
A displacement ellipsoid plot of (I), with the labelling scheme for the non-H atoms, which are drawn as 35% probability ellipsoids. Primes indicate the minor-site atoms.

from atom N1 to the carbonyl groups, leading to the development of negative charges on atoms O1 and O3. A similar pattern of bond lengths and angles has also been observed in other compounds containing the aminomethylene-1,3-diketone substructure (*e.g.* DeGarcia-Martin *et al.*, 1987), as revealed by a search of the Cambridge Structural Database (Allen *et al.*, 1983). Thus, the electronic structure of the title and related compounds can better be described by the azomethino-1,3-diketone rather than the aminomethylene tautomeric form. That the lone-pair electrons on atom N1 are delocalized through conjugation with the methylene-1,3-diketone moiety rather than the adjacent phenyl ring is also seen in the N1—C8 bond distance [1.421 (2) Å], which is not significantly different from the value [1.425 (3) Å] reported for a pure Nsp^2—Csp^2 single bond (Adler *et al.*, 1976). Even though the phenyl ring is deconjugated with the azomethino-1,3-diketone moiety, both fragments are roughly coplanar with one another; the C9—C8—N1—C7 torsion angle is −16.2 (4)°.

The charge distribution in the molecule can also be guessed from the formation of an intramolecular hydrogen bond between the N1—H1 donor and O2 acceptor (Table 2). Besides this hydrogen bond, there are several short intermolecular C—H···O contacts, which, on the basis of their H···O distances, can be regarded as weak hydrogen-bonding interactions (Table 2; Taylor & Kennard, 1982).

Experimental

The title compound, (I), was synthesized by a three-component reaction of equimolar amounts of aniline, triethyl orthoformate and cyclohexane-1,3-dione in ethanol under reflux, according to the method of Wolfbeis & Ziegler (1976) and described in detail by Marko *et al.* (2004). The product (m.p. 434 K) was recrystallized from ethanol to give single crystals suitable for X-ray analysis.

Crystal data

$C_{13}H_{13}NO_2$
$M_r = 215.24$
Triclinic, $P\overline{1}$
$a = 5.678$ (2) Å
$b = 8.424$ (3) Å
$c = 12.404$ (5) Å
$\alpha = 100.17$ (3)°
$\beta = 93.85$ (3)°
$\gamma = 107.96$ (4)°
$V = 550.8$ (4) Å^3
$Z = 2$
$D_x = 1.298$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
$\theta = 7$–20°
$\mu = 0.09$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.30 × 0.20 × 0.15 mm

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
4085 measured reflections
3188 independent reflections
1818 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\rm max} = 30.0°$
$h = -1 \rightarrow 7$
$k = -11 \rightarrow 11$
$l = -17 \rightarrow 17$
3 standard reflections every 97 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.065$
$wR(F^2) = 0.199$
$S = 1.05$
3188 reflections
178 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0636P)^2 + 0.2041P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.21$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—O1	1.257 (5)	C5—C6	1.520 (6)
C1—O1′	1.258 (7)	C7—N1	1.311 (2)
C1—C2	1.455 (3)	C8—C9	1.378 (3)
C1—C6	1.527 (6)	C8—C13	1.385 (3)
C2—C7	1.391 (3)	C8—N1	1.421 (2)
C2—C3	1.438 (3)	C9—C10	1.387 (3)
C3—O2	1.234 (2)	C10—C11	1.376 (3)
C3—C4	1.512 (3)	C11—C12	1.368 (3)
C4—C5	1.508 (4)	C12—C13	1.378 (3)
O1—C1—C2	121.2 (4)	O2—C3—C4	119.13 (19)
O1—C1—C6	121.8 (4)	C2—C3—C4	118.88 (18)
C2—C1—C6	116.9 (3)	C5—C4—C3	113.4 (2)
C7—C2—C3	121.58 (17)	C4—C5—C6	109.8 (5)
C7—C2—C1	116.70 (18)	C5—C6—C1	109.8 (5)
C3—C2—C1	121.69 (18)	N1—C7—C2	124.01 (18)
O2—C3—C2	121.99 (19)	C7—N1—C8	127.64 (17)
O1—C1—C2—C3	166.2 (4)	C3—C4—C5—C6	53.4 (6)
C6—C1—C2—C3	−9.5 (6)	C4—C5—C6—C1	−61.3 (8)
C7—C2—C3—O2	−1.6 (4)	O1—C1—C6—C5	−136.0 (6)
C7—C2—C3—C4	178.8 (2)	C2—C1—C6—C5	39.6 (9)
C1—C2—C3—C4	0.5 (4)	C3—C2—C7—N1	−0.1 (4)
O2—C3—C4—C5	157.5 (3)	C9—C8—N1—C7	−16.2 (4)
C2—C3—C4—C5	−22.9 (4)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.86	1.97	2.641 (3)	134
C7—H7···O1	0.93	2.41	2.749 (8)	102
C7—H7···O1′	0.93	2.46	2.780 (10)	100
C5—H5*A*···O1′$^{\rm i}$	0.97	2.27	3.006 (11)	132
C6′—H6′1···O1$^{\rm ii}$	0.97	2.47	3.196 (16)	131
C7—H7···O1$^{\rm iii}$	0.93	2.52	3.436 (6)	167
C7—H7···O1′$^{\rm iii}$	0.93	2.51	3.434 (8)	175
C9—H9···O1$^{\rm iii}$	0.93	2.41	3.317 (8)	166
C9—H9···O1′$^{\rm iii}$	0.93	2.49	3.332 (11)	151

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $-x, 1 - y, 1 - z$.

The disorder of the cyclohexane ring was modelled by resolving the positions of atoms C5, C6 and O1 into two components (C5/C5′, C6/C6′ and O1/O1′) and using a total of 35 restraints on corresponding bond distances and anisotropic displacement parameters [a combination of the DFIX and SIMU options in *SHELXL*97 (Sheldrick, 1997)]. The refined occupancies for the unprimed (major) and primed (minor) sites were 58.2 (6) and 41.8 (6)%, respectively. H atoms were treated as riding on their carrier atoms, with $U_{\rm iso}$(H) set at $1.2U_{\rm eq}$ of the parent atom.

Data collection: *XSCANS* (Siemens, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLUTON* (Spek, 1992); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1643). Services for accessing these data are described at the back of the journal.

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