Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O2	0.5910 (9)	0.3677 (3)	0.2409 (1)	0.019 (2)
O3'	0.5434 (9)	−0.0846 (3)	0.1547 (1)	0.020 (2)
O4'	0.5145 (9)	0.1900 (3)	0.1050 (1)	0.015 (2)
O5'	0.2877 (9)	0.1723 (3)	0.0002 (1)	0.020 (2)
N1	0.3061 (10)	0.3409 (4)	0.1671 (2)	0.014 (2)
N3	0.2985 (11)	0.5399 (4)	0.2176 (2)	0.016 (2)
N4	0.0036 (12)	0.7109 (4)	0.1951 (2)	0.018 (2)
C2	0.4042 (13)	0.4167 (5)	0.2099 (2)	0.015 (3)
C4	0.0967 (13)	0.5874 (5)	0.1843 (2)	0.014 (3)
C5	−0.0100 (13)	0.5144 (5)	0.1392 (2)	0.015 (3)
C51	−0.2254 (13)	0.5719 (5)	0.0992 (2)	0.017 (3)
C52	−0.0716 (15)	0.6589 (5)	0.0573 (2)	0.027 (3)
C6	0.0991 (13)	0.3917 (5)	0.1325 (2)	0.017 (3)
C1'	0.4154 (12)	0.2044 (5)	0.1597 (2)	0.012 (3)
C2'	0.1906 (13)	0.0953 (5)	0.1679 (2)	0.015 (3)
C3'	0.3030 (14)	−0.0143 (5)	0.1316 (2)	0.016 (3)
C4'	0.4129 (13)	0.0638 (5)	0.0836 (2)	0.013 (3)
C5'	0.1815 (13)	0.0893 (5)	0.0417 (2)	0.016 (3)
HO3'	0.471	−0.102	0.192	
HO5'	0.132	0.227	−0.017	
HN4B	0.102	0.775	0.220	

Table 2. *Selected geometric parameters* (Å, °)

O2—C2	1.255 (7)	N4—C4	1.339 (7)
O3'—C3'	1.432 (7)	C4—C5	1.425 (7)
O4'—C1'	1.439 (6)	C5—C51	1.517 (8)
O4'—C4'	1.450 (6)	C5—C6	1.341 (7)
O5'—C5'	1.413 (6)	C51—C52	1.533 (8)
N1—C2	1.384 (7)	C1'—C2'	1.520 (8)
N1—C6	1.380 (7)	C2'—C3'	1.514 (7)
N1—C1'	1.471 (6)	C3'—C4'	1.513 (7)
N3—C2	1.343 (6)	C4'—C5'	1.510 (8)
N3—C4	1.332 (7)		
C1'—O4'—C4'	109.3 (4)	C5—C51—C52	111.1 (5)
C2—N1—C6	120.0 (4)	N1—C6—C5	121.1 (5)
C2—N1—C1'	119.9 (4)	O4'—C1'—N1	108.7 (4)
C6—N1—C1'	120.1 (4)	O4'—C1'—C2'	105.7 (4)
C2—N3—C4	119.6 (4)	N1—C1'—C2'	114.9 (5)
O2—C2—N1	118.7 (4)	C1'—C2'—C3'	102.2 (4)
O2—C2—N3	121.4 (4)	O3'—C3'—C2'	112.5 (4)
N1—C2—N3	119.9 (5)	O3'—C3'—C4'	108.3 (5)
N3—C4—N4	115.5 (5)	C2'—C3'—C4'	101.9 (4)
N3—C4—C5	123.0 (5)	O4'—C4'—C3'	105.9 (4)
N4—C4—C5	121.5 (5)	O4'—C4'—C5'	109.3 (4)
C4—C5—C51	122.9 (5)	C3'—C4'—C5'	113.3 (5)
C4—C5—C6	116.2 (4)	O5'—C5'—C4'	111.1 (5)
C51—C5—C6	120.9 (4)		

Table 3. *Hydrogen-bonding geometry* (Å)

D—H$\cdots$A	H$\cdots$A	D$\cdots$A
O5'—HO5'$\cdots$O5'^{i}	2.08	2.78
O3'—HO3'$\cdots$O2^{ii}	1.72	2.71
N4—HN4B$\cdots$O2^{iii}	1.95	2.91

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

The H atoms attached to O5' and O3' were found in a difference synthesis map. All other H atoms were placed by the computer program. H-atom parameters were not refined. U_{iso} of each H atom was assigned as 0.01 Å^2 + U_{eq} of the atom to which it is covalently bonded.

Data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *NRCVAX TABLES* (Version of January 94).

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Two Centrosymmetric Conjugated Nitrones of the Diazabutadiene System

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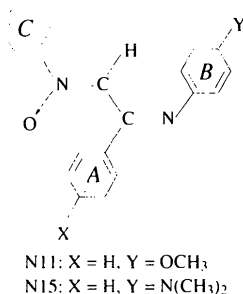
Abstract

The X-ray structures of N-[2-(4-methoxyphenylimino)-2-phenylethylidene]phenylamine N-oxide (N11), $C_{21}H_{18}N_2O_2$, and N-[2-{4-(N,N-dimethylamino)phenylimino}-2-phenylethylidene]phenylamine N-oxide (N15),

$C_{22}H_{21}N_3O$, both display a Z,Z configuration of the 1,4-diazabutadiene moiety with N=C—C=N torsion angles of $-123.5\,(2)$ and $141.4\,(4)°$ for N11 and N15, respectively. The aryl rings are twisted with respect to one another in both molecules. The crystal packing is controlled by very weak C—H···O hydrogen bonding, dipole coupling and van der Waals interactions.

Comment

The structures of the investigated compounds were determined as part of a structural study of 1,2,4-triaryl-1,4-diazabutadiene N^4-oxides having different X and Y substituents (see scheme below). This is the first presentation of nitrone crystal structures having an N=C—C=N→O arrangement.

N11: X = H, Y = OCH₃
N15: X = H, Y = N(CH₃)₂

The compounds were synthetized and characterized using MS, IR, UV, ^1H NMR (Moskal & Milart, 1984) and ^{13}C NMR (Moskal & Milart, 1985) spectroscopic techniques.

The molecular structures of compounds N11 and N15 with the atom-numbering schemes are shown in Figs. 1 and 2, respectively. Both nitrones reveal a Z,Z,s-E configuration of the 1,4-diazabutadiene fragment with the N(1)=C(7) double-bond length falling within the range found for three previously reported 1,4-diazabutadiene structures with the lone pair on the N atom [CEFCOF (Keijsper et al., 1983), DANVUJ and DANWAQ (Albano, Demartin, De Renzi, Morelli & Saporito, 1985)]. These were the only relevant structures in the Cambridge Structural Database (1992) up until 1992.

In the title compounds, the N(2)=C(14) double bonds are slightly lengthened due to the presence of the strongly electronegative O(1) atom of the nitrone group. The N(1)=C(7)—C(14)=N(2) fragment is not planar [torsion angle $-123.5\,(2)$ for N11 and $141.4\,(4)°$ for N15] and its conformation differs significantly from that found for the 1,4-dienes mentioned above, which were planar with torsion angles deviating from a *trans* conformation by less than 10°. A decrease in the conjugation between the carbon π electrons, expected for the observed non-planarity, results in the elongation of the C—C bond length of this moiety to $1.479\,(2)$ Å for N11 and $1.461\,(5)$ Å for N15. The
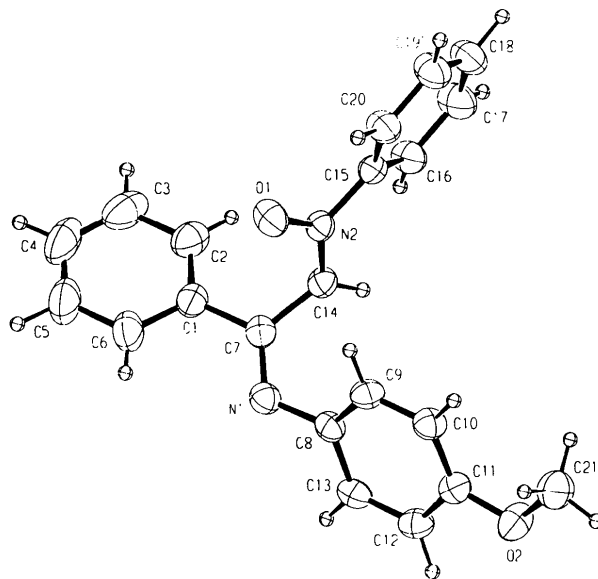
Fig. 1. *ORTEP*II (Johnson, 1976) view of the N11 molecule with displacement ellipsoids at the 40% probability level.
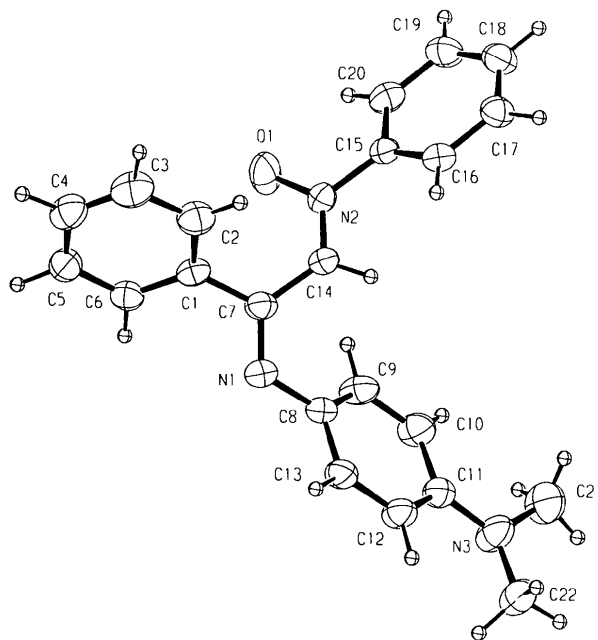
Fig. 2. *ORTEP*II (Johnson, 1976) view of the N15 molecule with displacement ellipsoids at the 40% probability level.

N(2)—O(1) bond length does not differ from similar values found in the Cambridge Structural Database (1992) for four structures containing the C=N(→O)—Ph fragment [CASTEV (Lobo et al., 1983), CIPWED (Greci & Sgarabotto, 1984), JIBFAB (Pritchard, Banks, DuBoisson & Tipping, 1991), TPNITR (Brown & Trefonas, 1973) and TPNITR01 (Falshaw, Hashi &

Taylor, 1985)] and, as is also seen in these structures, the O(1)—N(2)—C(15) angle is significantly less than 120°.

The whole molecule cannot achieve planarity mainly because of steric hindrance between the H atoms at C(14) and C(9) as well as between atom O(1) and the H atom at C(2), even though the observed distances are larger than the sum of the appropriate van der Waals radii [H(14)···H(9) 3.03 (3) for N11 and 2.68 (4) Å for N15, H(2)···O(1) 3.27 (3) for N11 and 3.18 (4) Å for N15].

Ring C makes an angle of 24.5 (1)° with the O(1), N(2), C(14) plane for N11 and 21.4 (2)° for N15. The O atom of compound N15 is involved in weak intramolecular hydrogen bonding [H(20)···O(1) 2.35 (3), C(20)···O(1) 2.699 (5) Å, C(20)—H(20)···O(1) 102 (2)°], whereas in compound N11 similar contacts are slightly longer [2.40 (4) and 2.715 (5) Å] due to the competing effect of the C(14)—H(14)···O(1)(x, $\frac{3}{2} - y$, $z - \frac{1}{2}$) intermolecular hydrogen bond [2.25 (2), 3.190 (2) Å, 162 (2)°].

Since the dihedral angle between ring B and the N(1), C(7), C(14), C(1) mean plane is very similar for both nitrones [48.7 (1) and 48.4 (1)° for N11 and N15, respectively], it seems that the π-electron system of the ring is conjugated to a certain degree both by the electron lone pair of the azomethine N(1) atom and the π electrons of the N(1)=C(7) double bond, this being independent of the nature of substituent Y.

Ring A is rotated about the C(1)—C(7) bond relative to the N(1), C(7), C(14) plane by 24.8 (1)° for N11 and 40.8 (2)° for N15. The change in conformation is probably caused by different intermolecular interactions.

The Gasteiger & Marsili (1980) charge calculation using the *CHEMX* program (Davies, 1991) gave dipole-moment values of 3.02 D for N11 and 3.48 D for N15. The dipole-moment vector is approximately parallel to the C(14)—C(7) bond in N11 and to the N(2)—O(1) bond in N15.

The strongly electron-donating N(CH₃)₂ group affects ring B in a more profound way then the OCH₃ substituent; the endocyclic angle at C(11) is significantly diminished in compound N15 [116.4 (3)°] compared to compound N11 [119.6 (2)°]. The electron lone pair of the N(CH₃)₂ substituent strongly polarizes the conjugated π-electron system of the molecule and causes a bathochromic shift of the absorption band. The cooperation between the amino N-atom lone pair and the π electrons is manifested in a deepening of the crystal colour.

The packing diagrams for compounds N11 and N15 are shown in Figs. 3 and 4, respectively. Molecules of N11, through C(14)—H(14)···O(1) hydrogen bonds, form layers perpendicular to the b axis of thickness $\frac{1}{2}b$. The shortest distances between the layers [H(18)···O(2)($-x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$) 2.56 (2) Å and
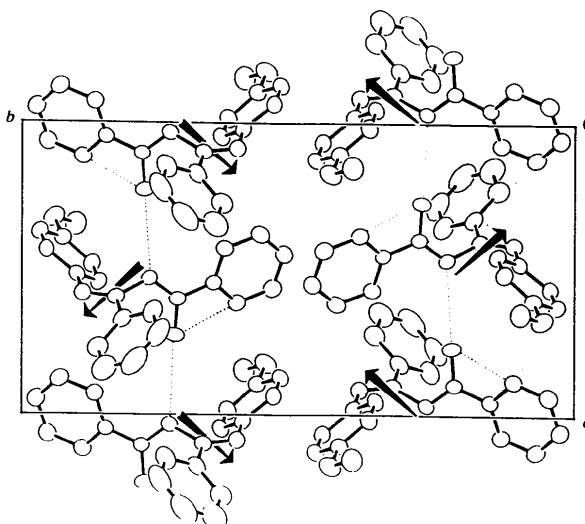

Fig. 3. Packing diagram of the N11 structure projected onto the bc plane. Only non-H atoms are shown. Possible hydrogen bonding [C(14)—H(14)···O(1)(x, $\frac{3}{2} - y$, $z - \frac{1}{2}$) and C(20)—H(20)···O(1)] is marked by dotted lines. Arrows present the dipole-moment vectors of the molecules with pointers towards negative charge. The angle between the C(14)—C(7) bond and the dipole-moment vector is about 11.9°.
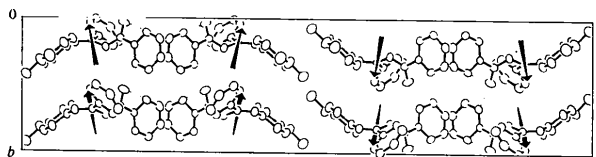

Fig. 4. The N15 unit cell projected onto the bc plane. H atoms are omitted. Shortest contacts suggesting C—H···O weak bonds [O(1)···H(16)—C(16)($\frac{1}{2} - x$, $y - \frac{1}{2}$, z) and C(20)—H(20)···O(1)] are marked by dotted lines. Arrows present the dipole-moment vectors of the molecules with pointers towards negative charge. The angle between the N(2)—O(1) bond and the dipole-moment vector is about 23.5°.

H(13)···H(212)($-x$, $2 - y$, $1 - z$) 2.54 (4) Å] correspond to weak van der Waals interactions and are longer then the shortest contact [H(17)···H(12)(x, $\frac{1}{2} - y$, $z + \frac{1}{2}$) 2.33 (3) Å]. As can be seen from Fig. 3, the layers are held together by coupling of the anti-parallel resultant dipoles.

The structure of compound N15 is also layered with four layers per unit cell perpendicular to the c axis. Within each layer the molecules are brought together by weak C—H···O hydrogen bonding [C(16)—H(16)···O(1)($\frac{1}{2} - x$, $y + \frac{1}{2}$, z) 2.46 (3), 3.238 (4) Å, 139 (2)°] and/or dipole attraction (see Fig. 4). The layers form pairs through the molecular dipoles coupling at $z = 0$ and $z = \frac{1}{2}$. The shortest resulting interlayer distances are H(12)···H(12)($1 - x$, $1 - y$, $1 - z$) 2.33 (5), H(223)···H(223)($2 - x$, $1 - y$, $1 - z$) 2.42 (8) and H(12)···H(222)($1 - x$, $1 - y$, $1 - z$) of 2.57 (6) Å. At $z = \frac{1}{4}$ and $z = \frac{3}{4}$ there are only very weak van

der Waals interactions between parallel layers with the shortest distance being $H(17)\cdots H(19)(1 - x, y + \frac{1}{2}, \frac{1}{2} - z)$ 2.70 (5) Å (appropriate sum of atomic radii is about 2.40 Å).

Experimental

Single crystals of both title compounds were obtained from ethanol solution by slow cooling.

Compound N11

Crystal data

$C_{21}H_{18}N_2O_2$
$M_r = 330.37$
Monoclinic
$P2_1/c$
$a = 8.6439$ (4) Å
$b = 19.5142$ (7) Å
$c = 10.5033$ (4) Å
$\beta = 101.723$ (4)°
$V = 1734.74$ (12) Å^3
$Z = 4$
$D_x = 1.265$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 33 reflections
$\theta = 8.7–26.1°$
$\mu = 0.658$ mm^{-1}
$T = 293$ (2) K
Plate
$0.3 \times 0.2 \times 0.1$ mm
Yellow

Data collection

Kuma Diffraction KM-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2630 measured reflections
2468 independent reflections
2468 observed reflections
$[I > 2\sigma(I)]$

$R_{int} = 0.0169$
$\theta_{max} = 78.00°$
$h = 0 \rightarrow 10$
$k = -24 \rightarrow 0$
$l = -13 \rightarrow 12$
3 standard reflections monitored every 50 reflections
intensity variation: <1.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0365$
$wR(F^2) = 0.0925$
$S = 1.057$
2468 reflections
299 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 0.2097P]$
where $P = (F_o^2 + 2F_c^2)/3$

$\Delta\rho_{max} = 0.152$ e Å^{-3}
$\Delta\rho_{min} = -0.149$ e Å^{-3}
Extinction correction: SHELXL
Extinction coefficient: 0.0136 (8)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Compound N15

Crystal data

$C_{22}H_{21}N_3O$
$M_r = 343.42$
Orthorhombic
Pbca
$a = 8.989$ (3) Å
$b = 9.6878$ (11) Å
$c = 41.670$ (4) Å
$V = 3628.8$ (13) Å^3
$Z = 8$
$D_x = 1.257$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 44 reflections
$\theta = 4.2–27.5°$
$\mu = 0.620$ mm^{-1}
$T = 293$ (2) K
Plate
$0.20 \times 0.15 \times 0.05$ mm
Red

Data collection

Kuma Diffraction KM-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1904 measured reflections
1447 independent reflections
1447 observed reflections
$[I > 2\sigma(I)]$

$R_{int} = 0.0452$
$\theta_{max} = 81.00°$
$h = -4 \rightarrow 9$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 48$
3 standard reflections monitored every 50 reflections
intensity variation: <2.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0432$
$wR(F^2) = 0.0852$
$S = 1.105$
1447 reflections
320 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 1.1826P]$
where $P = (F_o^2 + 2F_c^2)/3$

$\Delta\rho_{max} = 0.116$ e Å^{-3}
$\Delta\rho_{min} = -0.109$ e Å^{-3}
Extinction correction: SHELXL
Extinction coefficient: 0.00048 (9)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Compound N11				
C1	0.6795 (2)	0.81833 (9)	0.6739 (2)	0.0530 (4)
C2	0.7676 (2)	0.76267 (12)	0.6485 (2)	0.0676 (5)
C3	0.9182 (3)	0.7518 (2)	0.7220 (3)	0.0912 (8)
C4	0.9791 (3)	0.7961 (2)	0.8198 (3)	0.1074 (12)
C5	0.8937 (4)	0.8517 (2)	0.8453 (3)	0.1004 (9)
C6	0.7449 (3)	0.86331 (15)	0.7733 (2)	0.0724 (6)
C7	0.5170 (2)	0.83013 (8)	0.59751 (14)	0.0438 (3)
N1	0.4609 (2)	0.89105 (7)	0.58472 (13)	0.0481 (3)
C8	0.3015 (2)	0.90122 (7)	0.52076 (14)	0.0431 (3)
C9	0.1778 (2)	0.86182 (8)	0.5469 (2)	0.0476 (4)
C10	0.0231 (2)	0.87408 (8)	0.4845 (2)	0.0491 (4)
C11	−0.0093 (2)	0.92662 (8)	0.39455 (14)	0.0462 (4)
O2	−0.15631 (14)	0.94245 (7)	0.32514 (12)	0.0631 (4)
C21	−0.2868 (3)	0.90324 (13)	0.3481 (3)	0.0706 (6)
C12	0.1126 (2)	0.96870 (8)	0.3730 (2)	0.0492 (4)
C13	0.2659 (2)	0.95646 (8)	0.4352 (2)	0.0471 (4)
C14	0.4357 (2)	0.76903 (8)	0.53249 (14)	0.0428 (3)
N2	0.40868 (15)	0.71730 (6)	0.60288 (11)	0.0410 (3)
O1	0.4287 (2)	0.72197 (6)	0.72816 (10)	0.0590 (3)
C15	0.3542 (2)	0.65156 (8)	0.54636 (13)	0.0416 (3)
C16	0.2731 (2)	0.60950 (9)	0.6159 (2)	0.0537 (4)
C17	0.2221 (3)	0.54598 (10)	0.5649 (2)	0.0665 (5)
C18	0.2516 (3)	0.52525 (10)	0.4473 (2)	0.0693 (6)
C19	0.3326 (3)	0.56778 (10)	0.3789 (2)	0.0692 (6)
C20	0.3851 (2)	0.63139 (9)	0.4281 (2)	0.0546 (4)
Compound N15				
C1	0.0644 (4)	0.1446 (3)	0.36669 (7)	0.0437 (9)
C2	−0.0006 (5)	0.2137 (4)	0.34119 (8)	0.0571 (11)
C3	−0.1453 (5)	0.1804 (5)	0.33177 (10)	0.0657 (12)
C4	−0.2210 (5)	0.0762 (5)	0.34648 (9)	0.0628 (11)
C5	−0.1569 (4)	0.0053 (4)	0.37160 (8)	0.0543 (10)
C6	−0.0155 (4)	0.0403 (4)	0.38209 (8)	0.0473 (9)
C7	0.2157 (4)	0.1827 (3)	0.37828 (6)	0.0444 (9)
N1	0.2340 (3)	0.1903 (3)	0.40890 (5)	0.0490 (8)
C8	0.3751 (4)	0.2221 (4)	0.42233 (7)	0.0463 (9)
C9	0.5080 (5)	0.1627 (4)	0.41296 (8)	0.0564 (10)
C10	0.6397 (5)	0.1976 (4)	0.42774 (9)	0.0582 (11)
C11	0.6457 (4)	0.2927 (4)	0.45290 (7)	0.0490 (9)
C12	0.5108 (4)	0.3492 (4)	0.46260 (8)	0.0519 (10)

C13	0.3780(4)	0.3131(4)	0.44826(8)	0.0514(10)	C3—C4—C5	120.1(4)	O1—N2—C14	122.6(3)
C14	0.3277(4)	0.2236(4)	0.35472(7)	0.0480(10)	C4—C5—C6	120.0(4)	O1—N2—C15	115.5(2)
N2	0.3516(3)	0.1564(3)	0.32819(6)	0.0426(7)	C5—C6—C1	120.3(3)	C14—N2—C15	121.8(3)
O1	0.2895(3)	0.0393(2)	0.32197(6)	0.0686(8)	N1—C7—C14	124.2(3)	C16—C15—C20	120.6(3)
C15	0.4532(3)	0.2079(3)	0.30367(6)	0.0379(8)	N1—C7—C1	116.8(3)	C20—C15—N2	118.1(3)
C16	0.4890(4)	0.3460(4)	0.30174(7)	0.0440(8)	C14—C7—C1	118.6(3)	C15—C16—C17	119.0(3)
C17	0.5870(4)	0.3894(4)	0.27811(8)	0.0498(9)	C7—N1—C8	121.1(3)	C18—C17—C16	120.5(4)
C18	0.6453(5)	0.2964(4)	0.25648(8)	0.0553(10)	C9—C8—C13	117.8(3)	C19—C18—C17	120.1(4)
C19	0.6078(5)	0.1594(4)	0.25842(8)	0.0576(11)	C9—C8—N1	124.8(3)	C18—C19—C20	120.0(4)
C20	0.5119(5)	0.1145(4)	0.28210(7)	0.0501(10)	C13—C8—N1	117.3(3)	C19—C20—C15	119.8(4)
N3	0.7769(4)	0.3248(3)	0.46802(7)	0.0666(9)	C10—C9—C8	121.0(3)	C11—N3—C22	120.3(4)
C21	0.9181(6)	0.2919(7)	0.45298(14)	0.0777(14)	C9—C10—C11	122.1(4)	C11—N3—C21	120.2(3)
C22	0.7800(6)	0.4278(5)	0.49301(11)	0.0685(13)	N3—C11—C12	121.8(3)	C22—N3—C21	116.6(4)

C2—C1—C7—N1	136.3(3)	C7—C14—N2—C15	173.4(3)
C2—C1—C7—C14	−36.9(4)	O1—N2—C15—C16	158.7(3)
C14—C7—N1—C8	−8.9(5)	C20—C15—C16—C17	−1.0(5)
C9—C10—C11—N3	178.5(4)	N2—C15—C16—C17	179.5(3)
N1—C7—C14—N2	141.4(3)	C10—C11—N3—C22	177.4(4)
C1—C7—C14—N2	−45.9(5)	C10—C11—N3—C21	17.4(6)
C7—C14—N2—O1	−7.6(5)		

Table 2. *Selected geometric parameters* (Å, °)

Compound N11

C1—C2	1.384(3)	C11—O2	1.366(2)
C1—C6	1.393(3)	C11—C12	1.390(2)
C1—C7	1.487(2)	O2—C21	1.423(3)
C2—C3	1.388(3)	C12—C13	1.374(2)
C3—C4	1.363(5)	C14—N2	1.300(2)
C4—C5	1.368(5)	N2—O1	1.295(2)
C5—C6	1.372(3)	N2—C15	1.451(2)
C7—N1	1.281(2)	C15—C20	1.380(2)
C7—C14	1.479(2)	C15—C16	1.381(2)
N1—C8	1.419(2)	C16—C17	1.386(3)
C8—C9	1.389(2)	C17—C18	1.372(3)
C8—C13	1.397(2)	C18—C19	1.378(3)
C9—C10	1.385(2)	C19—C20	1.385(3)
C10—C11	1.384(2)		

C2—C1—C6	118.9(2)	O2—C11—C12	115.68(14)
C2—C1—C7	120.9(2)	C10—C11—C12	119.6(2)
C6—C1—C7	120.1(2)	C11—O2—C21	118.12(15)
C1—C2—C3	120.2(3)	C13—C12—C11	120.63(15)
C4—C3—C2	119.8(3)	C12—C13—C8	120.3(2)
C3—C4—C5	120.6(3)	N2—C14—C7	119.13(13)
C4—C5—C6	120.4(3)	O1—N2—C14	121.39(13)
C5—C6—C1	120.1(3)	O1—N2—C15	116.30(11)
N1—C7—C14	124.45(14)	C14—N2—C15	122.32(12)
N1—C7—C1	119.75(14)	C20—C15—C16	121.2(2)
C14—C7—C1	115.64(14)	C20—C15—N2	120.94(14)
C7—N1—C8	119.34(13)	C16—C15—N2	117.81(13)
C9—C8—C13	118.45(15)	C15—C16—C17	118.9(2)
C9—C8—N1	122.80(14)	C18—C17—C16	120.6(2)
C13—C8—N1	118.56(14)	C17—C18—C19	119.9(2)
C10—C9—C8	121.27(15)	C18—C19—C20	120.5(2)
C11—C10—C9	119.5(2)	C15—C20—C19	118.9(2)
O2—C11—C10	124.71(15)		

C2—C1—C7—N1	−153.3(2)	C1—C7—C14—N2	61.2(2)
C2—C1—C7—C14	22.3(2)	C7—C14—N2—O1	10.9(2)
C14—C7—N1—C8	10.0(2)	C7—C14—N2—C15	−169.39(14)
C9—C10—C11—O2	178.48(15)	O1—N2—C15—C20	−154.9(2)
C10—C11—O2—C21	1.3(3)	C14—N2—C15—C16	−155.8(2)
N1—C7—C14—N2	−123.5(2)	C20—C15—C16—C17	−0.2(3)

Compound N15

C1—C2	1.385(5)	C11—N3	1.373(4)
C1—C6	1.396(5)	C11—C12	1.390(5)
C1—C7	1.490(5)	C12—C13	1.380(5)
C2—C3	1.397(6)	C14—N2	1.301(4)
C3—C4	1.364(6)	N2—O1	1.290(3)
C4—C5	1.378(5)	N2—C15	1.458(4)
C5—C6	1.387(5)	C15—C16	1.378(5)
C7—N1	1.289(3)	C15—C20	1.381(4)
C7—C14	1.461(4)	C16—C17	1.386(5)
N1—C8	1.421(4)	C17—C18	1.378(5)
C8—C9	1.382(5)	C18—C19	1.371(5)
C8—C13	1.395(5)	C19—C20	1.381(5)
C9—C10	1.377(5)	N3—C22	1.442(5)
C10—C11	1.397(5)	N3—C21	1.451(6)

C2—C1—C6	119.1(4)	N3—C11—C10	121.8(3)
C2—C1—C7	120.9(3)	C12—C11—C10	116.4(4)
C6—C1—C7	120.0(3)	C13—C12—C11	121.9(3)
C1—C2—C3	119.8(4)	C12—C13—C8	120.8(4)
C4—C3—C2	120.7(4)	N2—C14—C7	123.3(3)

The intensity data were corrected for Lorentz and polarization effects. The structures were solved by direct methods using *SHELXS86* (Sheldrick, 1985) and refined by anisotropic full-matrix least squares on F^2 (*SHELXL93*; Sheldrick, 1993). All H atoms were found from subsequent difference Fourier syntheses and refined isotropically.

Data collection: Kuma Diffraction KM-4 software. Cell refinement: Kuma Diffraction KM-4 software. Data reduction: Kuma Diffraction KM-4 software. Software used to prepare material for publication: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, and torsion angles have been deposited with the IUCr (Reference: PA1117). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Phenyl-3-(3,4,5-trimethoxyphenyl)-1,3-propanedione

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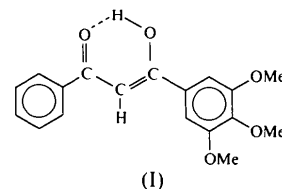(*Received* 18 *February* 1994; *accepted* 1 *July* 1994)

Abstract

The crystal structure of 1-phenyl-3-(3,4,5-trimethoxyphenyl)-1,3-propanedione, $C_{18}H_{18}O_5$, consists of discrete molecules separated by normal van der Waals interactions. The molecule exists in the enol form [*i.e.* 3-hydroxy-1-phenyl-3-(3,4,5-trimethoxyphenyl)propene-1-one] in the solid state, stabilized by a short intramolecular hydrogen bond.

Comment

β-Diketones have been studied intensively, specifically on the basis of their intramolecular hydrogen bonding in the enol form (Gilli, Bellucci, Ferretti & Bertolasi, 1989; Bertolasi, Gilli, Ferretti & Gilli, 1991). They form complexes with transition metal cations (Usha & Vijayan, 1989) as well as with the alkali earth metal cations Mg^{2+} (Hollander, Templeton & Zalkin, 1973*a*), Ca^{2+} (Hollander, Templeton & Zalkin, 1973*b*) and Sr^{2+} (Hollander, Templeton & Zalkin, 1973*c*). Crystal structures of dibenzoylmethanes have been reported as stable (Williams, 1966; Hollander, Templeton & Zalkin, 1973*d*; Jones, 1976; Kaitner & Meštrović, 1993) and metastable (Etter, Jahn, Urbańczyk-Lipkowska, 1987) polymorphs.

The title molecule (I) is almost planar. The terminal phenyl and trimethoxylated phenyl rings make torsion angles O9—C9—C10—C11 of −3.1 (3) and O7—C7—C1—C2 of 12.1 (3)°. The β-diketone–enol fragment O9—C9—C8—C7—O7—H7 is almost planar (O9—C9—C8—C7 −3.6, O7—C7—C8—C9 −0.8°). These values are not very different from those given for the symmetrical 1,3-diphenyl-1,3-propanedione enol (Hollander, Templeton & Zalkin, 1973*d*).

(I)

The β-diketone–enol group forms a very short intramolecular O7—H7···O9 hydrogen bond [O7···O9 2.508 (2) Å] which is in the range (2.432–2.554 Å) found for a series of dibenzoylmethanes (Bertolasi, Gilli, Ferretti & Gilli, 1991). Other dimensions of this hydrogen bond are O7—H7 1.11 (2), H7···O9 1.45 (2) Å and O7—H7···O9 155 (2)°. The position of the H7 atom is also confirmed by the C—O bond distances C7—O7 [1.303 (3) Å] and C9—O9 [1.278 (3) Å] and the C—C bond distances C8—C7 [1.373 (3) Å] and C8—C9 [1.414 (3) Å]. A view of the title molecule is presented in Fig. 1 and shows the atom-labelling scheme.
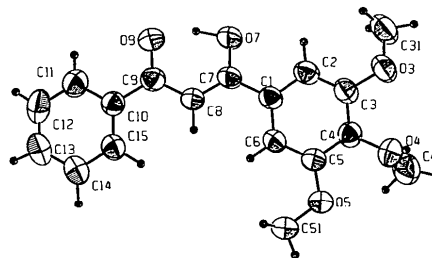

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule with the atom-labelling scheme (the displacement ellipsoids are drawn at 50% probability).

The enol structures of dibenzoylmethanes are similar to those of the chalcones, which often crystallize in non-centrosymmetric space groups and so have large non-linear optical properties (Zhengdong & Genbo, 1993). However, the title compound crystallizes in a centrosymmetric space group which is unfavourable for such optical properties.

Experimental

Crystal data

$C_{18}H_{18}O_5$	Mo $K\alpha$ radiation
$M_r = 314.34$	$\lambda = 0.71073$ Å