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(*E*,*E*)-1,4-Diethyl-1,4-diphenyl-2,3-diazabutadiene

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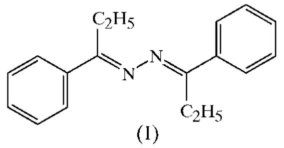
Molecules of the title compound [(*E*,*E*)-propiophenone azine], $C_{18}H_{20}N_2$, lie across centres of inversion in space group $P2_1/c$. The conformations of similar simple azines are discussed in terms of the soft hydrogen bonds present in the structures.

Comment

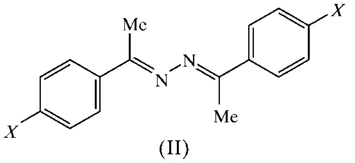
The title compound [(*E*,*E*)-propiophenone azine], (I), was synthesized as a potentially useful ligand for metal complexation. However, its molecular structure provides an interesting comparison both with the series of bis(4-substituted) acetophenone azines, (II*a*)–(II*f*) (Chen *et al.*, 1994*a*,*b*), and with benzophenone azine, (III) (Saha *et al.*, 1995).

Molecules of (I) lie across centres of inversion in space group $P2_1/c$, with the reference molecule centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) (Fig. 1). Consequently, the central C7—N1—N1^{i}—C7^{i} fragment [symmetry code: (i) $1 - x, 1 - y, 1 - z$] is strictly planar; indeed, with the exception of the terminal methyl groups, the whole molecule is almost planar as judged by the leading torsion angles (Table 1). Other intramolecular features of note are the clear distinction between the single and double bonds within the central spacer unit, the marked geometric distortion at the branching atom C7, shown by the bond angles at atom C7, and the rather small C—N—N bond angle.

The conformation of (I) is in marked contrast to the conformations of compounds (II*a*)–(II*d*), in which the C—N—N—C torsion angles range from 138.7 (2)° in (II*a*) to 124.6 (6)° in (II*d*), although molecules of (II*e*) are centrosymmetric, with a torsion angle of 180° (Chen *et al.*, 1994*b*). It was accordingly suggested (Chen *et al.*, 1994*b*) that this torsion angle is determined by the balance of substituent electronegativity and substituent π-acceptor capacity, with both strong π-acceptor substituents and strongly electronegative substituents tending to increase the torsion angle. However, this proposition does not readily accommodate the behaviour of (II*f*). This compound exhibits concomitant polymorphism (Bernstein *et al.*, 1999), with two monoclinic forms, in one of which ($Z' = \frac{1}{2}$ in $P2_1/c$) the molecules are centrosymmetric while in the other ($Z' = 1$ in $P2_1/n$) the C—N—N—C torsion angle is 142.8 (3)° (Chen *et al.*, 1994*a*). In (III), the molecules lie across twofold rotation axes in space group $A2/a$ (alternative setting of $C2/c$), with a C—N—N—C torsion angle of 132.5 (7)° (Saha *et al.*, 1995).

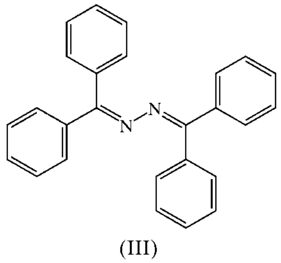


(I)



(II)

(*a*) X = H
(*b*) X = F
(*c*) X = Cl
(*d*) X = Br
(*e*) X = CN
(*f*) X = CH_3



(III)

In (I), which has H atoms at the 4-positions of the phenyl rings, the conformation is the same as that in the $Z' = \frac{1}{2}$ polymorph of the isomeric compound (II*f*) but differs from those in both (II*a*) and the $Z' = 1$ polymorph of (II*f*). While the electronic effects of the substituents at the 4-positions are doubtless of some importance, the analysis of Chen *et al.* (1994*b*) is formulated entirely on the basis that the conformation is solely determined by intramolecular factors; the analysis ignores entirely the possible influence of direction-specific interactions between the molecules. In the event, scrutiny of the atomic coordinates for (II*a*)–(II*d*), (II*f*) and (III) [deposited in the Cambridge Structural Database (Allen, 2002), although no coordinates are available for (II*e*)] shows that soft (Desiraju & Steiner, 1999) hydrogen bonds are present in (II*a*), (II*b*), (II*c*), (III) and the $Z' = 1$ polymorph of (II*f*) (Table 2). No such interactions are present in (I) or the centrosymmetric polymorph of (II*f*). Only for (II*d*) is a torsion angle other than 180° observed in the absence of direction-specific intermolecular interactions, suggesting that intermolecular factors may be at least as significant as intramolecular factors in determining the C—N—N—C torsion

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angles in compounds of this general type. Consistent with this result, we note that in the analogue of (II) having $X = \mathrm{OH}$, which crystallizes as a monohydrate in a structure containing both O—H⋯O and O—H⋯N hydrogen bonds, the C—N—N—C torsion angle is 148 (1)° (García-Mina *et al.*, 1982).

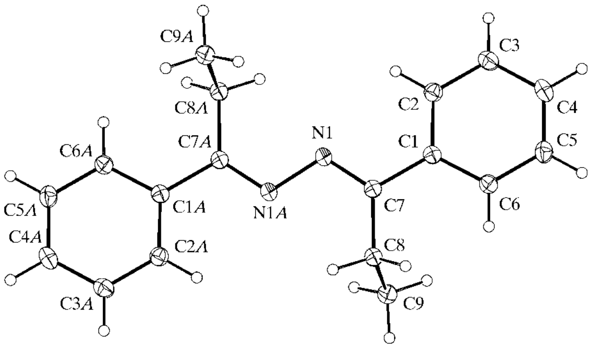

Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix *A* are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

Experimental

Compound (I) was prepared by heating under reflux an acidified ethanol solution of propiophenone and hydrazine hydrate (Fleming & Harley-Mason, 1961). Large crystals of (I) [m.p. 339–341 K; literature m.p. 339–340 K (Elguero *et al.*, 1968)] were deposited on cooling the reaction mixture, and a cubic block suitable for single-crystal X-ray diffraction was cut from one of the large crystals selected directly from the prepared sample.

Crystal data

$C_{18}H_{20}N_2$
$M_r = 264.36$
Monoclinic, $P2_1/c$
$a = 4.5985$ (2) Å
$b = 9.6973$ (5) Å
$c = 16.3968$ (8) Å
$\beta = 94.935$ (3)°
$V = 728.47$ (6) Å^3
$Z = 2$

$D_x = 1.205$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1656 reflections
$\theta = 3.3$–27.5°
$\mu = 0.07$ mm^{-1}
$T = 120$ (2) K
Block, yellow
0.10 × 0.10 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{\min} = 0.924$, $T_{\max} = 0.993$
3098 measured reflections
1656 independent reflections

1222 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 27.5°$
$h = -5 \rightarrow 5$
$k = -12 \rightarrow 12$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.116$
$S = 1.03$
1656 reflections
92 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0638P)^2 + 0.0449P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C7—N1	1.2917 (14)	N1—N1$^{\rm i}$	1.4056 (18)
N1—C7—C1	115.93 (10)	C1—C7—C8	119.29 (9)
N1—C7—C8	124.72 (10)	C7—N1—N1$^{\rm i}$	113.73 (11)
C2—C1—C7—N1	−1.29 (15)	C9—C8—C7—N1	96.31 (13)
C1—C7—N1—N1$^{\rm i}$	177.06 (10)	C8—C7—N1—N1$^{\rm i}$	−0.16 (17)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 2
Soft hydrogen-bond parameters (Å, °) for compounds (II) and (III).

The original atom labelling is used throughout. *Cg*1 is the centroid of ring C2–C7, *Cg*2 is the centroid of ring C10–C15, *Cg*3 is the centroid of ring C11–C16 and *Cg*4 is the centroid of ring C8–C13.

D—H⋯*A*	H⋯*A*	*D*⋯*A*	*D*—H⋯A
Compound (II*a*)			
C7—H5⋯*Cg*2$^{\rm ii}$	2.87	3.750 (2)	138
C12—H10⋯*Cg*1$^{\rm iii}$	2.86	3.693 (2)	134
C14—H12⋯*Cg*2$^{\rm iv}$	2.81	3.599 (2)	130
Compound (II*b*)			
C14—H10⋯F1	2.49	3.350 (3)	136
Compound (II*c*)			
C8—H5⋯*Cg*1$^{\rm vi}$	2.75	3.539 (2)	129
C11—H8⋯*Cg*1$^{\rm i}$	2.90	3.688 (2)	130
Compound (II*f*), $P2_1/n$ polymorph			
C3—H1⋯*Cg*1$^{\rm vii}$	2.97	3.686 (3)	124
C15—H13⋯*Cg*3$^{\rm viii}$	2.78	3.670 (3)	139
Compound (III)			
C12—H9⋯*Cg*4$^{\rm ix}$	2.99	3.733 (10)	126

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $-x, -y, 2 - z$; (iii) $-x, 1 - y, 2 - z$; (iv) $-\frac{1}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$; (v) $x, y, 1 + z$; (vi) $x, \frac{1}{2} - y, -\frac{1}{2} + z$; (vii) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (viii) $\frac{3}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$; (ix) $\frac{3}{2} - x, \frac{1}{2} - y, \frac{5}{2} - z$.

Space group $P2_1/c$ was assigned uniquely from the systematic absences. All H atoms were located from difference maps and thereafter treated as riding atoms, with C—H distances of 0.95 (aromatic), 0.98 (CH_3) and 0.99 Å (CH_2).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants that have provided computing facilities for this work and JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1202). Services for accessing these data are described at the back of the journal.

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