Table 2. *Bond lengths* (Å), *bond angles* (°) *and dihedral angles* (°)

P–C(1)	1·8511 (9)	P–C(4)	1·8525 (13)
C(1)–C(2)	1·5348 (12)	C(4)–C(5)	1·534 (2)
C(2)–C(3)	1·4713 (12)	C(5)–C(6)	1·469 (2)
C(3)–N(1)	1·1522 (12)	C(6)–N(2)	1·148 (2)
C(1)–H(11)	0·959 (13)	C(4)–H(4)	0·972 (14)
C(1)–H(12)	0·959 (13)		
C(2)–H(21)	0·974 (12)	C(5)–H(5)	0·95 (2)
C(2)–H(22)	0·982 (13)		
C(1)–P–C(1)′	96·79 (4)	C(1)–P–C(4)	103·17 (4)
P–C(1)–C(2)	113·61 (6)	P–C(4)–C(5)	117·39 (8)
C(1)–C(2)–C(3)	112·08 (7)	C(4)–C(5)–C(6)	111·0 (1)
C(2)–C(3)–N(1)	180 (1)	C(5)–C(6)–N(2)	178·7 (3)
P–C(1)–C(2)–C(3)	57·04 (8)	C(4)–P–C(1)–C(2)	73·54 (6)
C(1)–P–C(4)–C(5)	50·17 (2)		

Table 3. *Experimental differences between two structure determinations of* $P(CH_2CH_2CN)_3$

	100K[a]	298K[b]
a (Å)	6·597 (2)	6·812 (3)
b (Å)	12·761 (2)	12·988 (7)
c (Å)	5·9276 (14)	5·869 (2)
β (°)	90·95 (2)	91·08 (3)
Radiation	Mo	Cu
2 *θ* range (°)	0–80	0–115
Number of reflections used	2484	650
Number of variables	91	83
R	0·040	0·056
wR	0·045	0·094

(*a*) This work. (*b*) Cotton *et al.* (1981).

There are large differences between the molecular conformations in $P(CH_2CH_2CN)_3$ and $P(CH_2CN)_3$. The latter is a propeller-shaped molecule placed on a crystallographic threefold axis like $OP(CH_2CH_2CN)_3$ (Cotton *et al.*, 1981). It appears that arranging the side chains in $P(CH_2CN)_3$ in a conformation like that in $P(CH_2CH_2CN)_3$ would place two of the cyano groups in the molecule so close that this arrangement would be energetically unfavourable. Although dipole–dipole interactions influence the crystal packing in both $P(CH_2CH_2CN)_3$ and $P(CH_2CN)_3$ they lead to quite different molecular arrangements. In $P(CH_2CN)_3$ the dipoles are placed orthogonally whereas they are almost antiparallel in $P(CH_2CH_2CN)_3$.

Table 3 shows that the unit cell behaves strongly anisotropically on cooling. The remarkable increase of the *c* axis on cooling has been confirmed by our room-temperature photographs.

As no phase transition occurs between 298 K and 100 K we found it likely that the expansion of the *c* axis could have its origin in steric interactions. Inspection of the intermolecular contacts reveals that the interatomic distances are generally longer than the sum of the van der Waals radii. The only exceptions are the distances from N(1) to six surrounding methylene H atoms, which fall in the range 2·63–2·88 Å, compared with the sum of the van der Waals radii, 2·80 Å. A reduction of the *c* axis would diminish some of the N(1)–H distances and could lead to an energetically less favourable crystal packing.

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Structure of *syn*-9-Acetyl-1,6-imino-8,13-methano[14]annulene,* $C_{17}H_{15}NO$

By Riccardo Destro, Emanuele Ortoleva and Massimo Simonetta

Dipartimento di Chimica Fisica ed Elettrochimica e Centro CNR, Università, via Golgi 19, 20133 *Milano, Italy*

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Abstract. $M_r = 249·3$, monoclinic, space group $P2_1/n$, $a = 11·242$ (2), $b = 6·590$ (1), $c = 17·152$ (2) Å, $\beta = 97·88$ (1)°, $V = 1258·7$ (6) Å^3, $Z = 4$, $D_m = 1·30$, $D_x = 1·316$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·076$ mm^{-1}, $F(000) = 528$, $T = 298$ K. Final $R = 0·069$ for 2550 independent observed reflections. The

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* Alternative nomenclature: 4-acetyl-15-azatricyclo[8.4.1.1^{3,8}]-hexadeca-1,3,5,7,9,11,13-heptaene.

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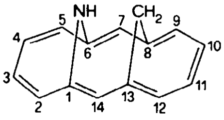
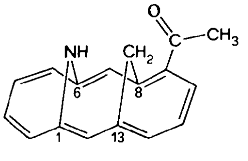
comparison of the molecular geometry of the unsubstituted *syn*-1,6-imino-8,13-methano[14]annulene with that of its derivative studied here suggests the presence of partial disorder in the crystals of the former compound.

Introduction. The results of the crystal-structure analysis of the unsubstituted *syn*-1,6-imino-8,13-methano[14]annulene, henceforth IMA, have been recently reported (Destro, Gavezzotti & Simonetta, 1982). That work included a detailed comparison of the molecular geometry of IMA with that of similar compounds with different bridging groups. None of the molecules considered for comparison carried substituent groups on the annulene perimeter, so that the observed differences in geometry could be referred to the nature and reciprocal influence of the bridging groups only.

On the whole, the molecular conformation of IMA was consistent with the expected steric effects of the $-NH-$ and $-CH_2-$ groups, but some geometrical features of the two bridging groups were rather unusual. To confirm these findings the study of the crystal structure of the title compound (hereinafter IMMCA) was undertaken.



IMA



IMMCA

Experimental. Sample of the substance kindly supplied by Professor E. Vogel. D_m measured (at room temperature) by flotation (diluted K_2HgI_4). Prismatic crystal of approximate dimensions 0·12 × 0·25 × 0·28 mm. CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. Lattice parameters from least-squares treatment of 25 accurately centered reflections. Systematic absences: $h0l$ with $(h+l)$ odd and $0k0$ with k odd. Intensity measurements by variable-rate ω-scan technique to a maximum 2θ value of 55°. 2875 (h 0–14, k 0–8, l −22–22) independent reflections collected, of which 325 with $I<0$ given zero weight. Variance $\sigma(F_o^2) = [\sigma^2(I_{\text{raw}}) + (p\, I_{\text{raw}})^2]^{1/2}/$Lp, where $\sigma(I_{\text{raw}})$ based on counting statistics, and $p = 0{\cdot}03$; Lp correction; no absorption correction. Three standard reflections (610, $\bar{1}3\bar{5}$, $\bar{1}21$) periodically checked, no deviation from average intensity $>3\sigma$. Structure solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971). H atoms located by difference maps. Full-matrix least-squares refinement (non-H atoms anisotropic, H isotropic) based on 2550 F's, 233 variables, including a secondary extinction coefficient [final value = 1·1 (1) × 10^{-6}mm^{-1}]. $w = 4F_o^2/\sigma^2(F_o^2)$; final $R = 0{\cdot}069$, $R_w = 0{\cdot}047$, $S = 1{\cdot}324$ [$R = 0{\cdot}038$, $R_w = 0{\cdot}040$ for 1648 reflections with $F_o^2 > 3\sigma(F_o^2)$]. Ratio of max. parameter shift to error = 0·24 (0·14 for non-H atoms). No peaks higher than 0·25 e Å^{-3} on final difference map. Scattering factors from *International Tables for X-ray Crystallography* (1974). *SDP* programs (Enraf–Nonius, 1979) used.

Discussion. Final atomic parameters are listed in Table 1. The atomic numbering scheme and bond lengths are reported on Fig. 1, while bond angles are given in Table 2.* A side view of the molecule is shown in Fig. 2, which includes the values of some relevant dihedral angles.

When compared with the molecular geometry of the unsubstituted parent compound IMA (Destro *et al.*, 1982), that of IMMCA shows a substantial similarity in the main features, so that the latter compound can be classified as 'aromatic' on the same grounds as the former. However, a closer inspection reveals some significant changes induced by the insertion of the $-COCH_3$ group on the annulene ring. They include (i) the closure of the bond angle C(8)—C(9)—C(10) from 125·6 (2)° in IMA to 120·7 (1)° here; (ii) the lengthening of the C(8)—C(9) bond distance [1·413 (3) Å in IMA *vs* 1·442 (2) Å in IMMCA]; and (iii) the change of the torsion angle C(7)—C(8)—C(9)—C(10) from −149·6 (2)° in IMA to −137·9 (1)° in IMMCA.

Table 1. *Final atomic positional parameters* (× 10^5) *and equivalent isotropic thermal parameters* (Å^2 × 10^2)

$$B_{\text{eq}} = \tfrac{4}{3}\sum\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
C(1)	23641 (15)	14153 (26)	5990 (10)	365 (4)
C(2)	34619 (16)	17097 (31)	3087 (10)	467 (4)
C(3)	36904 (15)	33580 (33)	−1366 (10)	485 (4)
C(4)	30808 (16)	52218 (32)	−1934 (9)	463 (4)
C(5)	21090 (15)	57866 (28)	1770 (9)	379 (4)
C(6)	13400 (13)	44065 (25)	4792 (8)	294 (3)
C(7)	6533 (13)	48541 (24)	10761 (8)	280 (3)
C(8)	777 (12)	34554 (23)	14985 (8)	269 (3)
C(9)	−3779 (13)	39349 (25)	22228 (8)	296 (3)
C(10)	−2259 (14)	25948 (28)	28522 (9)	372 (4)
C(11)	5720 (16)	9369 (28)	29926 (9)	418 (4)
C(12)	13391 (16)	1586 (27)	25152 (10)	408 (4)
C(13)	12483 (15)	5138 (24)	16961 (9)	339 (3)
C(14)	22566 (15)	4654 (26)	13123 (10)	383 (4)
C(15)	466 (14)	12310 (24)	13075 (8)	311 (3)
C(16)	−10550 (14)	58548 (26)	22832 (9)	337 (3)
C(17)	−14736 (17)	64350 (33)	30522 (11)	525 (5)
N	13358 (11)	23809 (21)	1644 (7)	336 (3)
O	−13049 (10)	69735 (19)	17163 (6)	428 (3)

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38649 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond angles* (°)

E.s.d.'s are about 0·1°.

C(1)–C(2)–C(3)	123·1	C(2)–C(1)–N	116·0
C(2)–C(3)–C(4)	127·2	C(14)–C(1)–N	119·6
C(3)–C(4)–C(5)	127·6	C(5)–C(6)–N	115·7
C(4)–C(5)–C(6)	124·0	C(7)–C(6)–N	119·8
C(5)–C(6)–C(7)	124·4		
C(6)–C(7)–C(8)	126·0	C(7)–C(8)–C(15)	122·3
C(7)–C(8)–C(9)	123·4	C(9)–C(8)–C(15)	113·7
C(8)–C(9)–C(10)	120·7	C(12)–C(13)–C(15)	115·6
C(9)–C(10)–C(11)	129·2	C(14)–C(13)–C(15)	122·8
C(10)–C(11)–C(12)	128·7		
C(11)–C(12)–C(13)	124·6	C(8)–C(9)–C(16)	119·5
C(12)–C(13)–C(14)	121·0	C(10)–C(9)–C(16)	119·8
C(13)–C(14)–C(1)	125·5	C(9)–C(16)–C(17)	120·0
C(14)–C(1)–C(2)	124·0	C(9)–C(16)–O	121·5
		C(17)–C(16)–O	118·5
C(1)–N–C(6)	104·8		
C(8)–C(15)–C(13)	102·6		

Table 3. *Comparison of geometries at the bridging groups in IMA and IMMCA*

	IMA	IMMCA
C(1)–N	1·463 (2) Å	1·436 (2) Å
C(6)–N	1·469 (2)	1·440 (2)
N–H(N)	1·11 (2)	0·87 (1)
C(1)–N–C(6)	105·9 (1)°	104·8 (1)°
C(8)–C(15)	1·480 (2) Å	1·501 (2) Å
C(13)–C(15)	1·491 (2)	1·499 (2)
C(15)–H(15*A*)	1·05 (2)	0·98 (1)
C(15)–H(15*B*)	0·95 (2)	0·97 (1)
C(8)–C(15)–C(13)	103·1 (1)°	102·6 (1)°
C(1)···C(6)	2·340 (3) Å	2·278 (2) Å
C(8)···C(13)	2·326 (3)	2·341 (2)

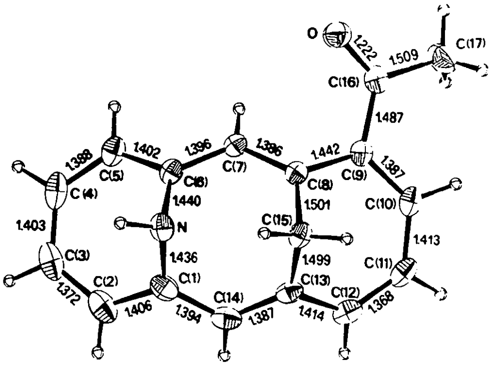

Fig. 1. The molecule seen along the direction corresponding to the maximum moment of inertia of the annulene nucleus. Thermal ellipsoids are drawn at a probability of 0·30. H atoms are on an arbitrary scale. Numbering scheme and bond lengths (Å) (e.s.d.'s of about 0·002 Å) are reported.

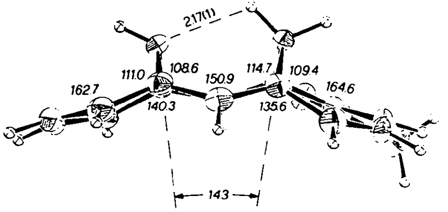

Fig. 2. Side view of the molecule, with dihedral angles (°) between least-squares planes (e.s.d.'s of about 0·01°) and a short N···H contact (Å).

Atoms C(9), C(16), C(17) and O are coplanar within 0·007 (1) Å; the least-squares plane defined by them makes a dihedral angle of 5·4 (1)° with the best plane passing through atoms C(8), C(9), C(10) and C(16). Such a value can be assumed as a measure of the deviation from coplanarity of the $-COCH_3$ group with the annulene ring. The intramolecular distance O···H(7), 2·51 (1) Å, and the intermolecular contact O···H(15*B*) (at *x*, 1 + *y*, *z*), 2·54 (1) Å, do not qualify as particularly short, while another intermolecular contact involving the O atom, O···H(N) (at −*x*, 1−*y*, −*z*), 2·39 (1) Å, suggests a very weak hydrogen bond. There are two more intermolecular distances (both with atoms at −*x*, 1−*y*, −*z*) less than the sum of van der Waals radii, namely C(6)···C(6), 3·322 (2) Å, and C(6)···C(7), 3·277 (1) Å. Although all the intermolecular contacts so far mentioned imply atoms of the bridging groups, we do not consider such interactions as responsible for the marked differences (see Table 3) between IMA and IMMCA at the bridge sites. Rather, the geometries suggest the possibility that partial disorder might be present in the crystals of IMA.

The results of the **TLS** analysis (Schomaker & Trueblood, 1968) are in agreement with this possibility. Indeed, (i) the least-squares treatment of the thermal factors of the C atoms of the annulene perimeter shows that for the 14-membered ring the fit to a rigid body is worse for IMA than for IMMCA, in spite of the presence of the $-COCH_3$ side group in the latter molecule; and (ii) the principal axes of libration are nearly along the principal axes of inertia in IMMCA, while in the case of IMA this occurs only for one of the three axes.

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