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1,3-Bis(phenylamino)indenium Perchlorate

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Abstract. $C_{21}H_{17}N_2^+.ClO_4^-$, $M_r = 396\cdot8$, orthorhombic, $Pc2_1b$, $a = 9\cdot072$ (1), $b = 12\cdot023$ (3), $c = 17\cdot172$ (3) Å, $V = 1872\cdot9$ Å^3, $Z = 4$, $D_x = 1\cdot41$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0\cdot71069$ Å, $\mu = 2\cdot2$ cm^{-1}, $F(000) = 824$, $T = 293$ K, $R = 0\cdot050$ for 801 observed data. In the indenium moiety the plane of the five-membered ring is inclined at $4\cdot1$ (8)° to the six-membered-ring plane. The bond lengths N(1)–C(7) 1·295 (10), C(7)–C(8) 1·404 (10), C(8)–C(9) 1·383 (11), C(9)–N(2) 1·303 (10), C(6)–C(7) 1·513 (11) and C(1)–C(9) 1·498 (11) Å show that the N(1),C(7),C(8),C(9),N(1) moiety is a delocalized system not conjugated with the aryl indenium ring. The aminophenyl rings are attached to the indenium moiety with the protons on both N atoms *trans* to the five-membered-ring proton; both rings are rotated around N–C(phenyl) bonds in opposite directions [torsion angles C(7)N(1)–C(11)C(16) 49 (1) and C(9)N(2)–C(21)C(22) −44 (1)°] so that the molecule has close to *m* symmetry. The cation is hydrogen-bonded to two symmetry-related anions *via* N–H···O hydrogen bonds [with N···O 2·913 (10) and 2·916 (10) Å]; in this way hydrogen-bonded chains are formed parallel to c.

Introduction. The 1-amino-3-iminoindenium cation, present in (I) as its *N,N'*-diphenyl derivative, contains in all-*trans* form the vinamidinium system which occurs all-*cis* in the 2,3-dihydro-1,4-diazepinium cation (II; $R = R' = H$) (Lloyd, Cleghorn & Marshall, 1974; Ferguson, Ruhl, Wieckowski, Lloyd & McNab, 1984), the geometry in both ring systems being relatively fixed. In (II) the vinamidinium system is delocalized and readily undergoes electrophilic substitution reactions, though reactivity in general is strongly influenced by steric factors (Lloyd *et al.*, 1974; Lloyd, McNab &

Marshall, 1975; Lloyd, Marshall & Tucker, 1981). The *N,N'*-dimethyl analogue of (I) behaves similarly to (II) but (I) itself is unreactive towards the same electrophiles. In contrast, *N*-phenyl groups in (II) do not prevent substitution, suggesting that the unreactivity of (I) is likely to be steric rather than electronic in origin.

(I)   (II)
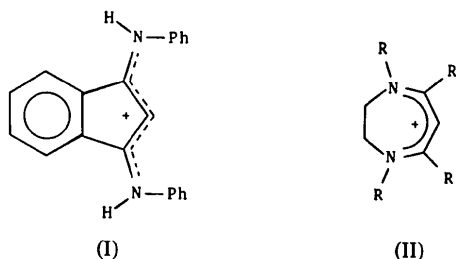
The intense deep-red colour of (I), compared with the yellow–orange colour of analogues which do not contain the indene aromatic ring, suggests conjugation between this ring and the vinamidinium cation system. This contrasts with (II) ($R' = \text{Ph}$), the properties of which do not suggest strong corresponding conjugation.

It is clearly of interest to determine the geometry of (I), and we report here the crystal structure of (I) as its perchlorate.

structure solution and refinement. For data collection $2 < \theta < 25°$ ($h\ 0$–10, $k\ 0$–14, $l\ 0$–20), ω–2θ scans, ω-scan width $(0\cdot70 + 0\cdot35\ \tan\theta)°$, intensities of three reflections monitored every hour of exposure time showed no significant decay. Lp corrections, 1732 unique reflections, 801 with $I > 3\sigma(I)$, where $\sigma^2(I)$ $= S + 2B + [0\cdot04(S - B)]^2$, $S =$ scan count and B = time-averaged background count, very few reflections with $\theta > 20°$, hence relatively low (46·2%) observed/ total reflection percentage. Absorption correction not considered necessary. Structure solved by heavy-atom method using NRC package (Gabe, Larson, Wang & Lee, 1981) and the PDP8 computer associated with the CAD-4 diffractometer. Refinement by block-diagonal least-squares calculations on F with anisotropic thermal parameters, H atoms from difference syntheses included at their idealized positions (C—H $1\cdot08$ Å) but not refined in subsequent calculations. Final $R = 0\cdot050$, $wR = 0\cdot033$ for 801 observed reflections, $R = 0\cdot131$ for all data; $w = 1/\sigma^2(F)$, $\Delta\rho\ \pm0\cdot2\ e\ \text{Å}^{-3}$. $(\Delta/\sigma)_{\max}$ $= 0\cdot11$ for x of C(21), $(\Delta/\sigma)_{\text{mean}} = 0\cdot04$. Atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965); allowance made for anomalous dispersion (Cromer & Liberman, 1970). Other computer programs used included $XANADU$ (Roberts & Sheldrick, 1975) and $ORTEP$II (Johnson, 1976).

Discussion. Final fractional coordinates with equivalent isotropic temperature factors are in Table 1. Table 2 contains molecular dimensions.* Our X-ray analysis unequivocally establishes the molecular structure of (I) as shown in Fig. 1 with our crystallographic numbering scheme.

In the indenium moiety of (I), both six- and five-membered rings are individually planar with maximum deviations of atoms from the least-squares planes being 0·012 (9) and 0·015 (9) Å respectively; the two planes are inclined at an angle of 4·1 (8)° to each other. The phenylamino substituents are attached to the indenium nucleus with protons on both N atoms *trans* to the C(8) proton and are rotated about N—C(phenyl) bonds in opposite directions [torsion angles C(7)N(1) —C(11)C(16) 49 (1) and C(9)N(2)—C(21)C(22) —44 (1)°].

The bond lengths in the N(1),C(7),C(8),C(9),N(2) moiety (Table 2) are entirely consistent with the delocalized formulation shown in (I). Thus the exocyclic C—N bonds [mean 1·299 (10) Å] and the C(7)—C(8) and C(8)—C(9) bonds [mean 1·394 (11) Å] are intermediate in length between single

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* Lists of structure factors, anisotropic thermal parameters, calculated H coordinates and the mean-plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42855 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final fractional coordinates and the mean* $B_{iso}(\text{Å}^2)$ $[=\frac{8}{3}\pi^2(U_{11} + U_{22} + U_{33})]$ *for* (I).ClO_4 *with e.s.d.'s in parentheses*

	x	y	z	B_{iso}
Cl	0·0541 (2)	0·9969*	0·2518 (1)	4·3 (1)
O(1)	0·1377 (6)	0·9983 (7)	0·3223 (3)	6·0 (4)
O(2)	0·1445 (10)	1·0109 (11)	0·1909 (4)	15·6 (10)
O(3)	−0·0563 (9)	1·0639 (10)	0·2581 (5)	19·0 (16)
O(4)	−0·0003 (14)	0·8915 (9)	0·2407 (7)	19·2 (11)
N(1)	0·2146 (7)	0·3808 (6)	0·4476 (3)	3·4 (4)
N(2)	0·5847 (6)	0·3850 (6)	0·6465 (4)	3·1 (4)
C(1)	0·5703 (7)	0·4635 (7)	0·5142 (4)	3·3 (7)
C(2)	0·7054 (8)	0·5102 (9)	0·5023 (4)	3·5 (5)
C(3)	0·7335 (9)	0·5615 (7)	0·4299 (5)	3·6 (5)
C(4)	0·6221 (9)	0·5640 (7)	0·3742 (5)	3·8 (5)
C(5)	0·4848 (9)	0·5153 (8)	0·3875 (4)	3·4 (5)
C(6)	0·4636 (8)	0·4646 (6)	0·4576 (4)	2·8 (5)
C(7)	0·3341 (8)	0·3974 (7)	0·4871 (4)	2·7 (5)
C(8)	0·3730 (8)	0·3604 (7)	0·5619 (4)	2·8 (5)
C(9)	0·5111 (9)	0·3995 (8)	0·5822 (4)	3·3 (5)
C(11)	0·0930 (8)	0·3135 (7)	0·4718 (4)	3·3 (5)
C(12)	0·0349 (8)	0·2367 (8)	0·4213 (4)	3·6 (5)
C(13)	−0·0828 (8)	0·1722 (8)	0·4466 (5)	4·3 (6)
C(14)	−0·1340 (10)	0·1760 (8)	0·5187 (5)	4·7 (6)
C(15)	−0·0783 (8)	0·2575 (8)	0·5684 (4)	4·6 (6)
C(16)	0·0356 (8)	0·3284 (7)	0·5466 (4)	3·1 (5)
C(21)	0·5297 (9)	0·3268 (8)	0·7146 (4)	3·5 (5)
C(22)	0·3872 (7)	0·3438 (7)	0·7425 (5)	3·7 (5)
C(23)	0·3446 (9)	0·2816 (8)	0·8073 (4)	4·4 (6)
C(24)	0·4339 (10)	0·2123 (8)	0·8442 (4)	4·7 (6)
C(25)	0·5781 (8)	0·1987 (8)	0·8169 (5)	4·2 (6)
C(26)	0·6257 (7)	0·2520 (10)	0·7526 (6)	4·1 (5)

* Fixed to define the origin.

Table 2. *Molecular dimensions for* (I).ClO_4

(a) Bond distances (Å)

C(1)–C(2)	1·364 (10)	C(12)–C(13)	1·390 (12)
C(1)–C(6)	1·372 (10)	C(13)–C(14)	1·323 (12)
C(1)–C(9)	1·498 (11)	C(14)–C(15)	1·395 (14)
C(2)–C(3)	1·412 (11)	C(15)–C(16)	1·391 (12)
C(3)–C(4)	1·391 (12)	N(2)–C(21)	1·450 (10)
C(4)–C(5)	1·395 (11)	C(21)–C(22)	1·395 (11)
C(5)–C(6)	1·363 (10)	C(21)–C(26)	1·412 (13)
C(6)–C(7)	1·513 (11)	C(22)–C(23)	1·395 (12)
C(7)–C(8)	1·404 (10)	C(23)–C(24)	1·325 (12)
C(7)–N(1)	1·295 (10)	C(24)–C(25)	1·399 (12)
C(8)–C(9)	1·383 (11)	C(25)–C(26)	1·348 (12)
C(9)–N(2)	1·303 (10)	Cl–O(1)	1·429 (6)
N(1)–C(11)	1·431 (10)	Cl–O(2)	1·340 (7)
C(11)–C(12)	1·371 (11)	Cl–O(3)	1·290 (8)
C(11)–C(16)	1·398 (10)	Cl–O(4)	1·373 (10)

(b) Bond angles (°)

C(2)–C(1)–C(6)	121·6 (7)	C(11)–C(12)–C(13)	118·3 (7)
C(2)–C(1)–C(9)	130·5 (7)	C(12)–C(13)–C(14)	122·9 (8)
C(6)–C(1)–C(9)	107·7 (6)	C(13)–C(14)–C(15)	118·1 (9)
C(1)–C(2)–C(3)	118·3 (7)	C(14)–C(15)–C(16)	122·3 (7)
C(2)–C(3)–C(4)	119·0 (7)	C(11)–C(16)–C(15)	116·5 (7)
C(3)–C(4)–C(5)	121·8 (7)	C(9)–N(2)–C(21)	124·9 (7)
C(4)–C(5)–C(6)	117·3 (7)	N(2)–C(21)–C(22)	121·7 (7)
C(1)–C(6)–C(5)	122·0 (7)	N(2)–C(21)–C(26)	117·9 (7)
C(1)–C(6)–C(7)	107·7 (6)	C(22)–C(21)–C(26)	120·4 (7)
C(5)–C(6)–C(7)	130·2 (7)	C(21)–C(22)–C(23)	116·9 (7)
C(6)–C(7)–C(8)	106·3 (6)	C(22)–C(23)–C(24)	123·4 (8)
C(6)–C(7)–N(1)	123·8 (7)	C(23)–C(24)–C(25)	119·0 (8)
C(8)–C(7)–N(1)	129·9 (7)	C(24)–C(25)–C(26)	121·3 (7)
C(7)–C(8)–C(9)	110·5 (7)	C(21)–C(26)–C(25)	118·9 (7)
C(1)–C(9)–C(8)	107·7 (6)	O(1)–Cl–O(2)	109·5 (5)
C(1)–C(9)–N(2)	123·1 (7)	O(1)–Cl–O(3)	109·5 (5)
C(8)–C(9)–N(2)	129·2 (7)	O(1)–Cl–O(4)	108·7 (6)
C(7)–N(1)–C(11)	125·5 (6)	O(2)–Cl–O(3)	117·5 (8)
N(1)–C(11)–C(12)	119·6 (7)	O(2)–Cl–O(4)	103·2 (8)
N(1)–C(11)–C(16)	118·8 (7)	O(3)–Cl–O(4)	108·0 (8)
C(12)–C(11)–C(16)	121·6 (7)		

and double bonds; the bonds linking this moiety to the indenium aromatic ring [C(6)—C(7) and C(1)—C(9), mean 1·506 (11) Å] are normal Csp^2—Csp^2 single bonds. They show no indication of higher bond order, and indeed may be slightly longer than expected (cf. 1·48 Å in 1,3-butadiene), suggesting a total absence of ground-state conjugation (Glidewell & Lloyd, 1982, 1984). The colour of the cation thus appears to be caused by effects in electronically excited states.
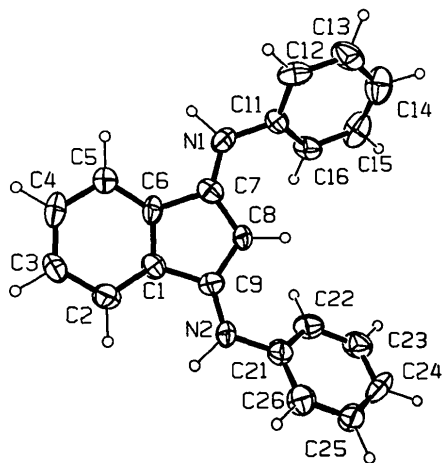

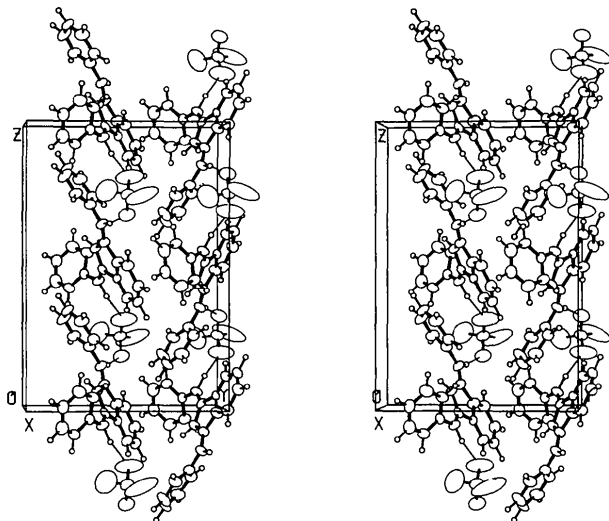Fig. 1. Molecular structure of the $[C_{21}H_{17}N_2]^+$ cation (I) with the crystallographic numbering scheme.

Fig. 2. Stereoview of the crystal packing of (1).ClO₄ showing hydrogen-bonded chains of the anions and cations, running parallel to the z axis.

Delocalization does not extend to the substituent phenyl rings; the relevant N—C distances [N(1)—C(11) and N(2)—C(21), mean 1·441 (10) Å] are indicative of single Csp^2—N bonds, and the phenyl rings are in any case rotated out of the relevant C—NH—C planes in opposite directions as noted above. This indicates that inhibition of electrophilic attack by the phenyl groups is probably steric. In normal indene systems where there are no resonance conjugation effects, the bond lengths in the five-membered ring show the expected single–double-bond-length alternation (e.g. Deppisch & Vittinghoff, 1980; Hanson, 1977; Dötz, Dietz, Kappenstein, Neugebauer & Schubert, 1979). The remaining bond lengths in the aromatic rings have the expected values, mean 1·380 (12) Å.

The cations are hydrogen-bonded to two symmetry-related anions [N(1)···O(2) 2·913 (10), H···O 1·87 and N(2)···O(1) 2·916 (10), H···O 1·86 Å] thus forming chains of alternating anions and cations running parallel to the z axis (Fig. 2); these chains are separated by normal van der Waals distances. Three of the perchlorate O atoms have large thermal parameters and the observed bond lengths associated with these atoms are much shorter than normal; this is commonly found in structures with loosely bound perchlorate ions.

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