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# Acetone *O*-[2-(1-Hydroxy-3-phenyl-2-triazeno)-2-propyl]oxime, $C_{12}H_{18}N_4O_2$*

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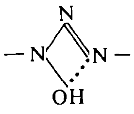
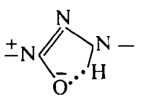
**Abstract.** $M_r = 250\cdot3$, monoclinic, $P2_1/c$, $a = 10\cdot391\ (1)$, $b = 13\cdot257\ (4)$, $c = 10\cdot321\ (2)$ Å, $\beta = 97\cdot78\ (1)^\circ$, $V = 1408\cdot5$ Å$^3$, $Z = 4$, $D_x = 1\cdot18$, $D_m = 1\cdot14$ Mg m$^{-3}$, m.p. 418 K, Ni-filtered Cu $K\alpha$, $\lambda(K\alpha_1) = 1\cdot54051$ Å, $\mu = 6\cdot01$ mm$^{-1}$, room temperature, $F(000) = 536$, $R = 0\cdot084$ for 1181 reflections. The structure analysis clearly indicates the presence of an intramolecular hydrogen bond and an N—H bond [N(1)—H(N1) = 1·05 (6) Å], supporting the existence of a resonance hybrid of two valence-bond contributors in the solid state. Marked electron delocalization has been observed in the C—N—N—N chain.

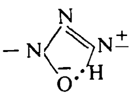
**Introduction.** The present study is related to our investigation of tautomerism in arylazobis(acetoximes). These compounds are a potentially useful class of organic reagents having extensive chemical applications (Bhargava & Sogani, 1971). Their complexing ability with metal ions is now well established (Elkins & Hunter, 1940; Chakraborti & Majumdar, 1977). An intramolecular hydrogen-bonded structure with tautomeric forms (I) and (II) is postulated for such compounds from the acid dissociation constants and from ultraviolet absorption studies (Purohit & Sogani, 1964; Purohit, Dugar & Sogani, 1965). The present study describes the crystal structure of the title compound (PBA).



(I)



(II*a*)



(II*b*)

**Experimental.** PBA synthesized following the general procedure of Bhargava & Sogani (1971). $D_m$: bromobenzene–kerosene mixture. Small white needles (from alcohol in presence of activated charcoal). Crystal 0·25 × 0·25 × 0·50 mm. Enraf–Nonius CAD-4 single-crystal diffractometer. Lattice parameters from 25 reflections ($30^\circ < 2\theta < 60^\circ$). Data collection: $h, k, \pm l$ with $2\theta \leq 120^\circ$, $\omega$–$2\theta$ scan mode, scan angle $\Delta 2\theta = (0\cdot75 + 0\cdot45\tan\theta)^\circ$, aperture width $(2\cdot00 + 0\cdot20\tan\theta)$ mm. Three standard reflections every 2000 s (3·5% variation). 1361 independent, 1181 with $F > 3\sigma(F)$. Absorption and decay corrections not applied. $P2_1/c$, general positions: $\pm(x, y, z;\ x, \tfrac{1}{2} - y, \tfrac{1}{2} + z)$ from systematic absences $0k0$, $k \neq 2n$ and $h0l$, $l \neq 2n$. Direct methods [*SHELX*76 (Sheldrick, 1976); 128 $E > 1\cdot27$]. Anisotropic block-diagonal refinement on $F$; H from $\Delta F$ synthesis, isotropic; final cycle: 235 parameters; $R = 0\cdot084$, $R_w = 0\cdot092$. $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 1/\sigma^2(F_o)$. Final $\Delta F$ map featureless. $(\Delta/\sigma)_{\max} = 0\cdot2$. All calculations with the *SHELX*76 programs. Atomic scattering factors from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965).

**Discussion.** The final fractional coordinates and equivalent isotropic thermal parameters are listed in Table 1 and follow the atom-numbering scheme shown in Fig. 1.†

A perspective view of the molecule is shown in Fig. 2. The distances and angles observed in the phenyl ring of PBA (Table 2) fall within the normal range, with mean bond length 1·377 (11) Å. The apparent change in the bond lengths of different methyl groups might be due to the strong thermal vibrations of C(11) and C(12).

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* NCL communication No. 3366.

† Lists of structure factors, anisotropic thermal parameters and some least-squares-plane details have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39178 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Considerable double-bond character in the N(2)—N(3) bond is evidenced by the short bond distance of 1·274 (7) Å and by the planarity of the bonding about N(3) indicating $sp^2$ hybridization. The presence of the N(1)—H(N1)···O(1) intramolecular hydrogen bond in the molecule clearly proves the existence of the resonance hybrid of the two valence-bond contributors in the solid state as shown in structures (II*a*) and (II*b*). The presence of the *N*-oxide structure supports the zwitterion character of the molecule suggested from a comparison of the intramolecular N—O and C—N bond distances.

Marked electron delocalization has been observed in the C—N—N—N chain. As mentioned by Burke-Laing & Laing (1976), the presence of the N(H) group and intramolecular hydrogen bonding seems to aid in the delocalization of $\pi$ electrons. Similar observations were made on the structure of diaminobenzene (Gladkova & Kondrashev, 1972).

We wish to thank Professor D. N. Purohit for his interest in this work.

Table 1. *Positional parameters of PBA (fractional coordinates for* O, N, C $\times 10^4$, *for* H $\times 10^3$) *and* $B_{eq}$ ( $= \frac{1}{3}\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$) *values*

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| O(1) | 9541 (4) | −90 (3) | 8459 (4) | 2·03 (7) |
| O(2) | 8345 (4) | −996 (3) | 6231 (4) | 2·12 (7) |
| N(1) | 8096 (5) | 668 (4) | 9918 (4) | 1·98 (7) |
| N(2) | 7551 (5) | 483 (4) | 8687 (5) | 1·99 (7) |
| N(3) | 8353 (5) | 103 (3) | 7992 (5) | 1·99 (7) |
| N(4) | 7697 (6) | −1757 (4) | 6908 (6) | 2·05 (8) |
| C(1) | 5993 (8) | 1200 (5) | 10472 (7) | 2·13 (7) |
| C(2) | 5271 (9) | 1639 (7) | 11349 (9) | 3·54 (8) |
| C(3) | 5868 (9) | 1993 (6) | 12529 (8) | 3·51 (8) |
| C(4) | 7188 (9) | 1926 (5) | 12820 (6) | 2·11 (7) |
| C(5) | 7924 (7) | 1479 (5) | 11960 (6) | 2·06 (7) |
| C(6) | 7316 (6) | 1115 (4) | 10765 (5) | 1·99 (8) |
| C(7) | 7924 (7) | −46 (5) | 6564 (6) | 2·01 (6) |
| C(8) | 8762 (12) | 706 (7) | 5861 (9) | 3·50 (7) |
| C(9) | 6500 (11) | 123 (9) | 6199 (8) | 3·51 (6) |
| C(10) | 7975 (9) | −2633 (8) | 6561 (13) | 3·56 (7) |
| C(11) | 8907 (20) | −2808 (12) | 5575 (17) | 5·79 (11) |
| C(12) | 7439 (11) | −3493 (7) | 7176 (12) | 5·69 (10) |
| H(N1) | 909 (6) | 53 (5) | 992 (6) | |

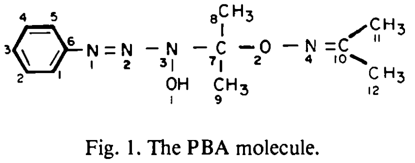

Fig. 1. The PBA molecule.

Table 2. *Intramolecular interatomic distances* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| C(1)—C(2) | 1·380 (12) | N(1)—C(6) | 1·401 (7) |
| C(1)—C(6) | 1·372 (10) | N(1)—N(2) | 1·342 (7) |
| C(2)—C(3) | 1·372 (12) | N(2)—N(3) | 1·274 (7) |
| C(3)—C(4) | 1·367 (13) | N(3)—O(1) | 1·289 (7) |
| C(4)—C(5) | 1·381 (10) | N(3)—C(7) | 1·494 (8) |
| C(5)—C(6) | 1·394 (8) | C(7)—C(8) | 1·565 (13) |
| C(7)—C(9) | 1·493 (13) | O(2)—C(7) | 1·391 (8) |
| O(2)—N(4) | 1·444 (7) | N(4)—C(10) | 1·260 (12) |
| C(10)—C(11) | 1·514 (22) | C(10)—C(12) | 1·452 (15) |
| N(1)—H(N1) | 1·05 (6) | | |
| C(2)—C(1)—C(6) | 120·5 (7) | C(1)—C(2)—C(3) | 120·4 (8) |
| C(2)—C(3)—C(4) | 119·5 (8) | C(3)—C(4)—C(5) | 120·9 (7) |
| C(4)—C(5)—C(6) | 119·5 (6) | C(5)—C(6)—C(1) | 119·2 (6) |
| C(5)—C(6)—N(1) | 117·8 (5) | N(1)—C(6)—C(1) | 122·9 (5) |
| C(6)—N(1)—N(2) | 117·5 (5) | N(1)—N(2)—N(3) | 112·4 (5) |
| N(2)—N(3)—O(1) | 122·3 (5) | O(1)—N(3)—C(7) | 119·0 (5) |
| N(2)—N(3)—C(7) | 118·5 (5) | O(2)—C(7)—N(3) | 107·5 (5) |
| O(2)—C(7)—C(8) | 104·4 (6) | O(2)—C(7)—C(9) | 114·0 (6) |
| N(3)—C(7)—C(8) | 105·2 (6) | N(3)—C(7)—C(9) | 112·5 (6) |
| C(8)—C(7)—C(9) | 112·5 (7) | N(4)—O(2)—C(7) | 109·3 (4) |
| O(2)—N(4)—C(10) | 111·5 (7) | N(4)—C(10)—C(11) | 121·6 (9) |
| N(4)—C(10)—C(12) | 118·9 (9) | C(11)—C(10)—C(12) | 119·4 (9) |
| N(1)—H(N1)···O(1) | 106·7 | | |

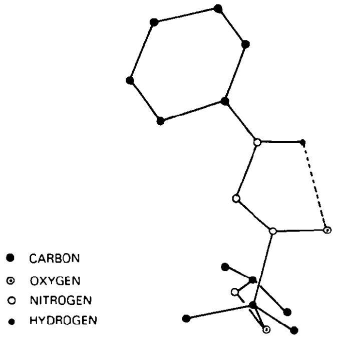

Fig. 2. The crystal structure of the PBA molecule viewed down the *b* axis.

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