

ments of the framework atoms and place changing of the Li atoms.

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The Crystal and Molecular Structure of 1-*p*-Tolyl-3-(α -cyano)benzylidenetriazene, C₁₅H₁₂N₄*

By J. W. SCHILLING† AND C. E. NORDMAN

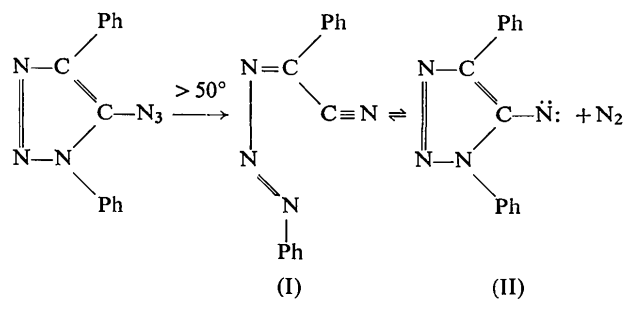
Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48104, U.S.A.

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The compound 1-*p*-tolyl-3-(α -cyano)benzylidenetriazene, C₁₅H₁₂N₄, is a product of the thermal decomposition of 1-*p*-tolyl-4-phenyl-5-azidotriazole, crystallizing from petroleum ether in the monoclinic space group *Pc* with $a = 4.036$ (2), $b = 11.109$ (2), $c = 14.805$ (8) Å, $\beta = 93.57$ (6)°, and two molecules per cell. 1019 reflections were recorded by the integrating oscillation and integrating Weissenberg techniques. The structure was solved by the vector search method from a sharpened Patterson function assuming the existence of the *p*-toluidyl skeleton, C₇N. The final value of $R = \sum |F_{\text{obs}} - F_{\text{calc}}| / \sum |F_{\text{obs}}|$ after refinement by full-matrix least-squares methods is 0.077. In previously determined aromatic triazene structures, R₁-N=N-N-(R₂,R₃), the triazene moiety usually displays equivalent N-N bond distances (of about 1.25 Å) when R₂ or R₃ is hydrogen or when the triazenido anion is acting as a bidentate ligand to a transition metal cation; in this structure neither R₂ nor R₃ is hydrogen and the N-N distances are nonequivalent (1.24 and 1.40 Å). This study is inconclusive regarding the hypothesis of Smith, Krbecek & Resemann [*J. Amer. Chem. Soc.* (1964), **86**, 2025] (based on its chemical reactions) that C₁₅H₁₂N₄ occurs in solution in an equilibrium between the title compound and a closed-ring nitrene.

Introduction

A product, C₁₄H₁₀N₄, of unknown structure, obtained from the thermal decomposition of 1,4-diphenyl-5-azidotriazole, was thought to exist in solution as an equilibrium mixture of the open chain triazene (I) and a stable nitrene (II):



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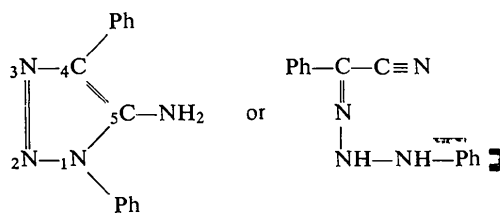
† Present address: Department of Molecular Biophysics and Biochemistry, Yale University, New Haven, Connecticut 06520, U.S.A.

(Smith, Krbecek & Resemann, 1964). The compound crystallizes very readily from a variety of nonpolar solvents in the orthorhombic space group *Pbca* with $a = 27.6$, $b = 11.4$, $c = 7.82$ Å; $Z = 8$.

A structure analysis was undertaken by the vector-search method (Nordman, 1966; Nordman & Schilling, 1970; Schilling, 1970a) upon an analogue, C₁₅H₁₂N₄, the product of 1-*p*-tolyl-4-phenyl-5-azidotriazole. This substance [compound (III), M.W. 248.31] displays the same chemical properties and would suffice to confirm the proposed structure, but since it crystallizes in space group *Pc*, only a one-dimensional determination of fragment location is required (*i.e.* with respect to the glide plane) rather than the three-dimensional location required in space group *Pbca*. The possibilities for the structure of (III) are analogous to (I) and (II) above, and will be designated CH₃-(I) and CH₃-(II).

A variety of possible structures were eliminated by Smith *et al.* on the basis of physical and chemical properties, but the positive evidence for the structure was inconclusive. C₁₄H₁₀N₄ and C₁₅H₁₂N₄ are dark red in color. The infrared spectrum normally exhibits no bands higher than 1600 cm⁻¹, but under certain conditions a weak band at 2200 cm⁻¹ occurs, suggesting the existence of a cyano group. The n.m.r. spectrum of C₁₄H₁₀N₄ shows six aromatic hydrogen atoms and two pairs of hydrogens at 1.75 and 2.1 τ ; the former are

as far downfield as aromatic hydrogen atoms *ortho* to an electron-withdrawing group; they are not *para* hydrogen atoms, since the same pair occurs in C₁₅H₁₂N₄. Reduction by various means, with the uptake of one mole of hydrogen, gives the amine corresponding to the starting material, or with cold dithionite, its open-chain isomer:



Smith *et al.* proposed an equilibrium between I and II, because some chemical reactions in which the N(1)-C(5) bond appears intact in the products would not be expected to arise from I and yet the infrared band at 2200 cm⁻¹ implies the existence of the nitrile. The analogous pyrazole system behaves similarly (Smith, Breen, Hajek & Awang, 1970) but reduction of the product analogous to (III) produces an open-chain intermediate product which progresses to the cyclic product. However, it is possible to produce an azo dimer of the closed-ring pyrazole analogue by heating the latter under very specific conditions, leading these authors to infer a (possibly small) concentration of the cyclic form.

Experimental

Crystals of C₁₅H₁₂N₄, slowly grown from petroleum ether, are dark red and tend to be either needle-like (with *a* along the needle) or chunky with few well defined faces; the latter are prone to display pronounced diffuse reflection. The space group was uniquely determined as *Pc* from the systematic absence of reflections *h*0*l* with *l* odd, and from a strikingly positive pyroelectricity test. The lattice parameters were determined by a least-squares fit to 19 observations of high-angle reflections utilizing the Cu *K*(α_1 - α_2) splitting observed in back-reflection oscillation photographs. Crystal data are as follows:

Space group *Pc*; *a* = 4.036 (2), *b* = 11.109 (2),
c = 14.805 (8) Å,
 β = 93.57 (6)°; μ = 6.28 cm⁻¹ (for Cu *K* α);
V = 662.51 Å³; *F*(000) = 260.

The crystal density was observed by flotation in potassium tartrate solution to be 1.23; *d*(calc) = 1.245. From the molecular weight, cell dimensions and crystal density, *Z* was determined as 2.

Intensity data were collected at room temperature using nickel-filtered Cu *K* α radiation (λ = 1.5418 Å). A crystal was mounted about *a* for integrated equi-inclination Weissenberg photographs (nets *nkl*, *n* = 0, 1, 2, 3), and a second crystal about *b* for integrated

general-inclination oscillation photographs. Since the integrating motion of the film was inadequate in the axial direction when the needle axis *a* was along the spindle, only tangential integration was used in the Weissenberg photographs. The needle was of approximately constant radius (0.25 × 1.5 mm), and so the resulting peak heights were taken as proportional to the integrated intensities. For the data collected about *b*, the crystal size was 0.7 × 0.5 × 1.0 mm; the inclination angle, μ , was 25°. In all cases five layers of Ilford G X-ray film were used. The intensities were recorded on a Joyce-Loebl microdensitometer. The oscillation data were corrected for the variation in obliquity of the diffracted beams by the method of Cox & Shaw (1930). Raw intensities were placed on a common scale by an algorithm which determines the logarithmic average of the scales of the individual datasets (Norman, 1960). No absorption correction was made. The Lorentz-polarization factor was applied, and the scale factor, *K* (applied to *F*_{obs}) and overall anisotropic thermal parameters β_{ij} were determined by a modification of Wilson's method (Schilling, 1968). Table 1 compares values determined by Wilson statistics with *a posteriori* values of the Wilson parameters based on structure-factor least-squares calculations. The latter were determined after the final structure refinement by setting all individual atom thermal parameters to zero and refining overall anisotropic thermal parameters plus scale factor; and similarly for the overall isotropic temperature factor.

Table 1. Overall thermal parameters

	Wilson methods		<i>A posteriori</i>
	Isotropic*	Anisotropic	structure-factor least-squares method
<i>B</i> (Å ²)	5.23	—	4.98 (8)
β_{11}	0.081	0.096	0.093 (2)
β_{22}	0.0106	0.0099	0.0102 (2)
β_{33}	0.0060	0.0053	0.0044 (1)
β_{13}	0.0014	0.0054	0.0065 (5)
<i>K</i>	0.1621	0.1633	0.184 (3)

* Values of β_{ij} in this column are those equivalent to isotropic motion.

Structure determination

Patterson coefficients for reflections '*m*' were computed as:

$$C_m = (Q_m F_{\text{obs}}^2 - \sum_k Z_k^2) \exp[-D(\sin \theta_m / \lambda)^2]$$

where

$$Q = K^2 \sum_j Z_j^2 / (\sum_j f_j^2) \exp(-\sum_j h_j h_j \beta_{1j}).$$

The factor *D* is a damping parameter, chosen to be zero. The Patterson function was computed at the points of a 60 × 60 × 60 grid; negative values of the Patterson function were set to zero. All searches used

Table 3 (cont.)

Hydrogen atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
H(1)	-0.248 (27)	0.163 (10)	0.071 (8)	7.0 (2.6)
H(2)	-0.429 (20)	0.207 (6)	0.252 (5)	4.2 (1.4)
H(3)	-0.175 (34)	0.416 (12)	0.390 (10)	3.7 (2.9)
H(4)	-0.522 (21)	0.321 (6) ¹	0.372 (5)	4.8 (1.3)
H(5)	-0.406 (23)	0.430 (8) ¹	0.387 (6)	5.6 (1.7)
H(6)	-0.031 (24)	0.519 (8) ¹	0.251 (7)	5.6 (2.0)
H(7)	0.148 (36)	0.572 (12)	0.116 (10)	8.8 (3.9)
H(8)	0.434 (16)	0.328 (6)	-0.266 (4)	2.4 (1.1)
H(9)	0.596 (23)	0.331 (8)	-0.412 (6)	6.2 (1.8)
H(10)	0.562 (20)	0.124 (6)	-0.517 (5)	3.2 (1.4)
H(11)	0.252 (18)	-0.050 (7)	-0.434 (5)	4.9 (1.6)
H(12)	0.117 (12)	-0.011 (5)	-0.284 (3)	1.0 (8)

with the 146 unobserved reflections given zero weight. The quantity minimized was $\sum w_i |F_o - F_c|^2$. Form factors for C and N were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); those for H were those of Stewart, Davidson & Simpson (1965). In the later stages of refinement, the Fortran II *ORFLS* program (Busing, Martin & Levy, 1962) was used; a special algorithm for computing the least-squares matrix was incorporated to permit

full-matrix refinement of up to 230 parameters on the IBM 7090 computer (Schilling, 1970*b*).

The origin was fixed by holding *x* and *z* for the nitrogen atom of the *p*-toluidyl group constant. Refinement by diagonal least-squares methods brought $R \equiv \sum |F_o - F_c| / \sum |F_o|$ to 0.125. The twelve hydrogen atoms were then found by a difference Fourier synthesis. *R* was reduced to 0.077 by further least-squares refinement with all 55 heavy-atom space parameters and scale factor in one block, the 114 heavy-atom anisotropic thermal parameters and scale factor in a second, and scale factor plus hydrogen space and isotropic thermal parameters in a third, refined on alternate cycles. The penultimate cycle refined all heavy atom parameters and scale factor in a single block, *i.e.* holding the hydrogen atom parameters constant.

A final full-matrix cycle refining all 218 parameters (the above atomic parameters plus scale factor) made no change in *R* for the 1019 observed reflections, but increased the error estimates on heavy-atom space parameters by as much as 25%. The largest shifts on this cycle were 1σ for the *y* coordinate of C(5) and 2σ for the temperature factor of H(3). A plot of $K^2 F_o^2 G$ versus $\ln |F_c / KF_o|$ where $G = (1 + \cos^2 2\theta) / \sin 2\theta$ (Nordman, 1962) for the strongest reflections showed no

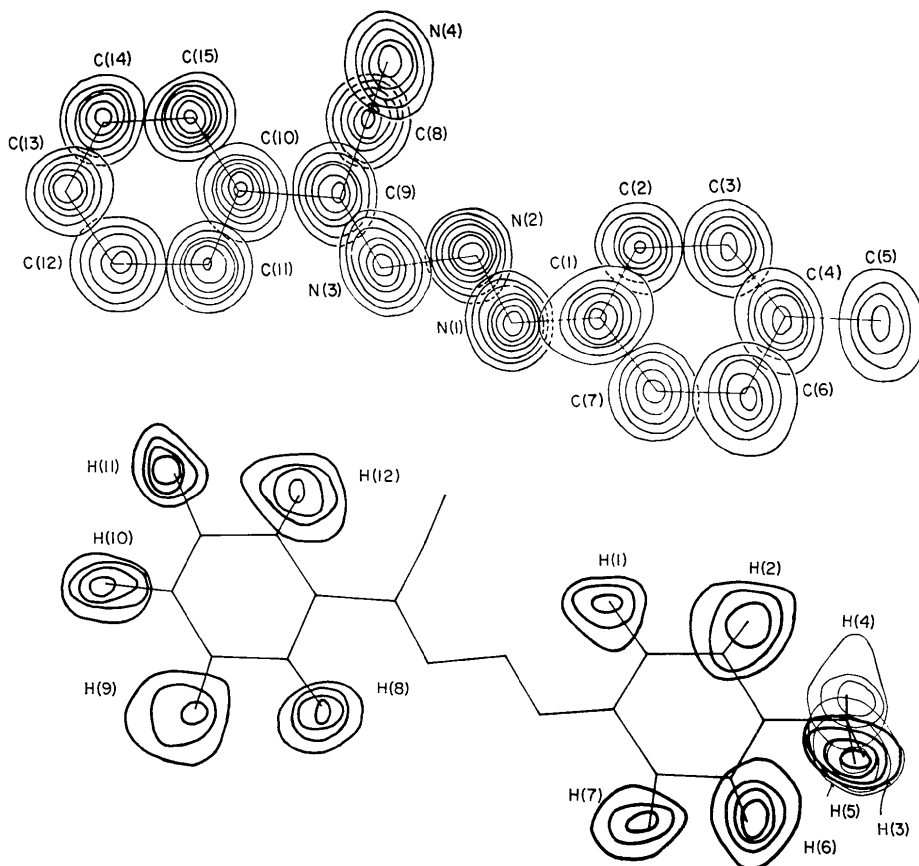


Fig. 1. Fourier syntheses. Carbon and nitrogen atoms from final Fourier synthesis, contours at $1 \text{ e.}\text{\AA}^{-3}$, zero contour omitted; hydrogen atoms from final ΔF synthesis, contour interval $\frac{1}{2} \text{ e.}\text{\AA}^{-3}$, zero contour omitted.

evidence of secondary extinction in the data. The final difference Fourier synthesis showed four peaks (in chemically implausible locations) of slightly less than the height of the lowest hydrogen. The least prominent hydrogen atoms (Fig. 1) are probably poorly determined. Further full-matrix refinement with a fixed, reasonable value of B for the hydrogen atoms would probably improve the determination of these atoms, but this was not felt to be sufficient reason to justify the cost. The twelve aromatic C-C distances in this molecule have an average value of 1.385 Å, with an r.m.s. deviation of 0.020 Å from that value.

Table 2 gives observed and calculated structure factors. Maximum values are given as FO for unobserved reflections. Fig. 1 shows the final Fourier syntheses of the C, N and H atoms.

Structure

Table 3 gives the final space and thermal parameters for atoms in one molecule. The thermal parameters

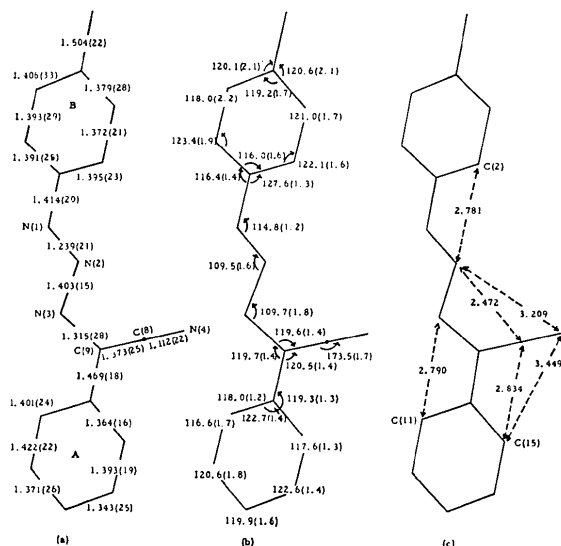


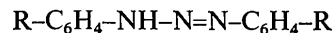
Fig. 2. Geometry of the 1-*p*-tolyl-3-(α -cyano)benzylidene-triazene molecule. (a) Bond distances (Å); (b) Bond angles (°); (c) Non-bonded intramolecular contacts (Å).

correspond to the expression:

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + kl\beta_{23} + hl\beta_{13})].$$

The e.s.d. (based upon the inverse least-squares matrix) of each parameter is given in parentheses, applying to the last significant figure. Atom naming is as in Fig. 1. Since the space group symmetry permits the origin to be arbitrarily specified in x and z , only the y parameter of N(1) was varied. Fig. 2 gives bond distances and angles with e.s.d.'s.

In aromatic triazene ('diazamine') crystal structures of the form



the two N-N distances are generally found to be equivalent within experimental error. The same is true if only one of the phenyls is substituted, eliminating the possibility that disorder of the symmetrically substituted triazene causes a pseudoequivalence of the bonds. A difference Fourier on the structure of the unsymmetrical *p*-methyl and on the symmetrical *p*-dimethyl derivative showed two half-hydrogen peaks on the intermolecular N-N vector (Kondrashev, 1969), indicating an equilibrium between tautomeric forms. Kondrashev and co-workers succeeded in biasing this tautomerism by multiple substitution of one of the phenyls. The resulting bond parameters of the triazene moiety in various derivatives are given in Table 4 [names as given in the translated papers: compound (IV), *p*-dibromodiazaminobenzene, Kondrashev, 1962; (V), *p*-bromodiazaniline, Omel'chenko & Kondrashev, 1967; (VI), 2,4-dibromodiazaminobenzene, Omel'chenko & Kondrashev, 1966]. A similar structure is the copper (I) complex of diazaminobenzene [(VII) in Table 4; Brown & Dunitz, 1961] in which the N-N distances are also found to be equivalent. The present structure (III) resembles (VI) in the triazene bond parameters.

There is a tendency in all of these structures for angles analogous to N(1)-C(1)-C(2) to be distorted by as much as 5° from the expected 120° and in (III) the deviation (ring B) is 7.6°; this is probably due to the unsymmetrical intramolecular contact N(2)-C(2)

Table 4. Bond parameters of the triazene moiety for $\text{C}_{15}\text{H}_{12}\text{N}_4$ and related structures

Compound	R ₁ -N(1)-N(2)-N(3)-R ₄				Angle				
	R ₁	R ₂	R ₃	R ₄	R ₁ -N(1)	N(1)-N(2)	N(2)-N(3)	N(3)-R ₄	N(1)-N(2)-N(3)
(III)	CH ₃ C ₆ H ₄ -	-	-	C ₆ H ₅	1.414 (20)Å	1.239 (21)Å	1.403 (15)Å	1.315 (28)Å	109.5 (1.6)°
(IV)	BrC ₆ H ₄ -	½H	½H	BrC ₆ H ₄ -	1.46	1.25	1.23	1.44	113
(V)	C ₆ H ₅ -	½H	½H	BrC ₆ H ₄ -	1.45	1.27	1.25	1.47	115
(VI)	C ₆ H ₅ -	-	H	Br ₂ C ₆ H ₃ -	1.42	1.25	1.45	1.43	107.7
(VII)	C ₆ H ₅ -	½Cu ⁺	½Cu ⁺	C ₆ H ₅ -	1.39 (3)	1.27 (3)	1.32 (3)	1.48 (3)	115.8 (2.0)

(Fig. 2c); the corresponding angle for ring *A* is nearly 120° because the intramolecular contacts are balanced. There are no intermolecular contacts to rings *A* or *B* closer than 3.8 Å. The three angles in the triazene moiety are not significantly different from those in (VII); the angle N(2)–N(1)–C(1) is similar to the N–N–C angle, 113.6°, in *trans*-azobenzene (Brown, 1966). The distance N(1)–C(1), 1.41, is shorter than in *trans*-azobenzene [1.433 (3) Å], but this difference (2 σ) is only marginally significant. Nevertheless, a shortening would be reasonable in view of the increased opportunity for delocalization of electrons. It is tempting to put compound (III) at the end of a sequence of analogues in which *trans*-azobenzene would be intermediate, and *cis*-azobenzene (Hampson & Robertson, 1941) would be at the opposite extreme; in the latter, steric crowding drastically inhibits delocalization (N–C distance, 1.46 Å). The bond distance N(2)–N(3), 1.403 Å is shorter than in (VI), in which it is 1.45 Å, because in (III) it is adjacent to the C(9)=N(3) bond. The distance N(1)=N(2) is quite comparable to that (1.243 Å) found in *trans*-azobenzene.

A least-squares plane was computed using the algorithm of Schomaker, Waser, Marsh & Bergman (1959) with iterative weighting based upon the standard deviations of the atomic coordinates and their projections upon a unit vector normal to the plane on each cycle. The molecule as a whole is very nearly planar, the largest deviation [C(5)] being 0.2 Å and three more being greater than 0.09 Å. There are no intermolecular contacts less than 3.9 Å to C(5). Rings *A* and *B* are rotated 8.2 and 8.8° respectively, with respect to the plane defined by the three triazene nitrogen atoms.

The distance C(8)–N(4) is shorter by 3 σ than the 1.14 Å usually observed for nitrile bonds, but a thermal motion correction would increase it somewhat. The nitrile angle C(9)–C(8)–N(4) deviates by 6.5° (8 σ) from 180°, probably because of an intermolecular contact of 3.4 Å between N(4) and C(13) in a glide-related molecule. There are also two close intramolecular contacts involving N(2); 2.472 Å to C(8) and 3.209 Å to N(4) (Fig. 2). The deviation of N(4) from a least-squares plane through the eight atoms C(8), C(9) and ring *A* is 0.113 Å.

The proposed equilibrium between CH₃–(I) and CH₃–(II) would have led one to expect CH₃–(I) to be found in the *cis* conformation, possibly co-crystallized with CH₃–(II). However, model-building indicates that the *cis* isomer may be less stable because of a close

contact between C(8) and N(1) (<2.8 Å if the molecule is planar) which would preclude planarity and inhibit delocalization. In solution, the *trans* form probably predominates. This study provides no support for the existence of a stable nitrene, but does not rule out the possibility that a small amount of this form is present in solution.

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