THE PHOTOCYCLIZATION OF A HYDRAZONE TO AN INDAZOLE

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Summary

UV irradiation of thin films of *p*-diethylaminobenzaldehyde diphenyl-hydrazone (1) produces 1-phenyl-3-(4-diethylamino-1-phenyl)-1,3-indazole (2) as the major photoproduct. A proposed mechanism for the reaction, which involves a photocyclization followed by an oxidation, is similar to the photocyclization of diphenylamine to carbazole and stilbene to phenanthrene. In order to gain more insight into the solid state photoreaction, an X-ray crystal structure analysis was performed on 1 to determine the geometry of the diphenylamine group relative to the hydrazone moiety. An X-ray structural analysis was also attempted for 2. In this case, however, owing to problems associated with crystal growth, we could establish the structure only qualitatively.

1. Introduction

During the course of our photochemical studies on compounds of both theoretical [1] and technological [2] importance we decided to examine the solid state photochemistry of a series of benzaldehyde hydrazones. We found that the solid state photochemistry of the hydrazones appeared to be different from their solution photochemistry and that *p*-diethylaminobenz-aldehyde diphenylhydrazone (DEH) (1) underwent a remarkable photo-chemical rearrangement. The photochemistry of DEH is the subject of this paper.
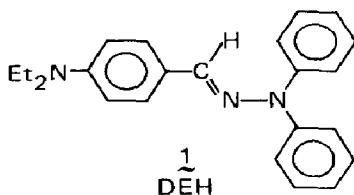
2. Results and discussion

Irradiation of thin films of DEH in air by a Pyrex-filtered 450 W Hanovia medium pressure lamp produced one major photoproduct 2. When the reaction was carried out in a system that permitted direct monitoring of the reaction course by IR spectroscopy, a quantitative conversion of DEH to 2 was observed. This sequence is shown in Figs. 1(a) - (e) and should be compared with the IR spectrum of 2 shown in Fig. 2. Significant changes have occurred in the spectral regions characteristic of the phenyl rings at about 1600 and 700 cm^{-1}.

Comparison of the ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of DEH and 2 showed that the diethylamino group was intact (Fig. 3). From the number of non-equivalent carbon atoms in the ^{13}C NMR spectrum, it was concluded that the diphenylamine portion of DEH had been altered. The mass spectrum of 2 displayed a molecular ion peak at $m/e = 341$ which indicated that two hydrogen atoms had been lost from DEH.

The structure most consistent with the spectral data was 1-phenyl-3-(4-diethylamino-1-phenyl)-1,3-indazole (2).

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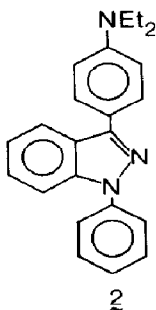
In order to identify the photoproduct unequivocally, crystals were prepared and an X-ray structure analysis was performed (see Section 3). Indazole 2 contained eight molecules per unit cell with two different orientations (Fig. 4). This complication, coupled with our inability to grow crystals of 2 that could be used for a quantitative structure analysis, allowed only a qualitative structural analysis. However, the qualitative X-ray structural analysis permitted unambiguous identification of the chemical structure for 2, and combined with the IR, NMR and mass spectroscopic analysis, we feel the identity assignment of 2 to an indazole is on a firm basis.

When the photolysis of DEH was carried out *in vacuo* and followed using IR spectroscopy, a different photoproduct (3) was observed that was partially converted to 2 on exposure to oxygen. We therefore propose the mechanism shown in Scheme 1. Photolysis of DEH leads to a photoproduct 3 (whose chemical structure is postulated) which is oxidized to indazole 2 on exposure to oxygen.
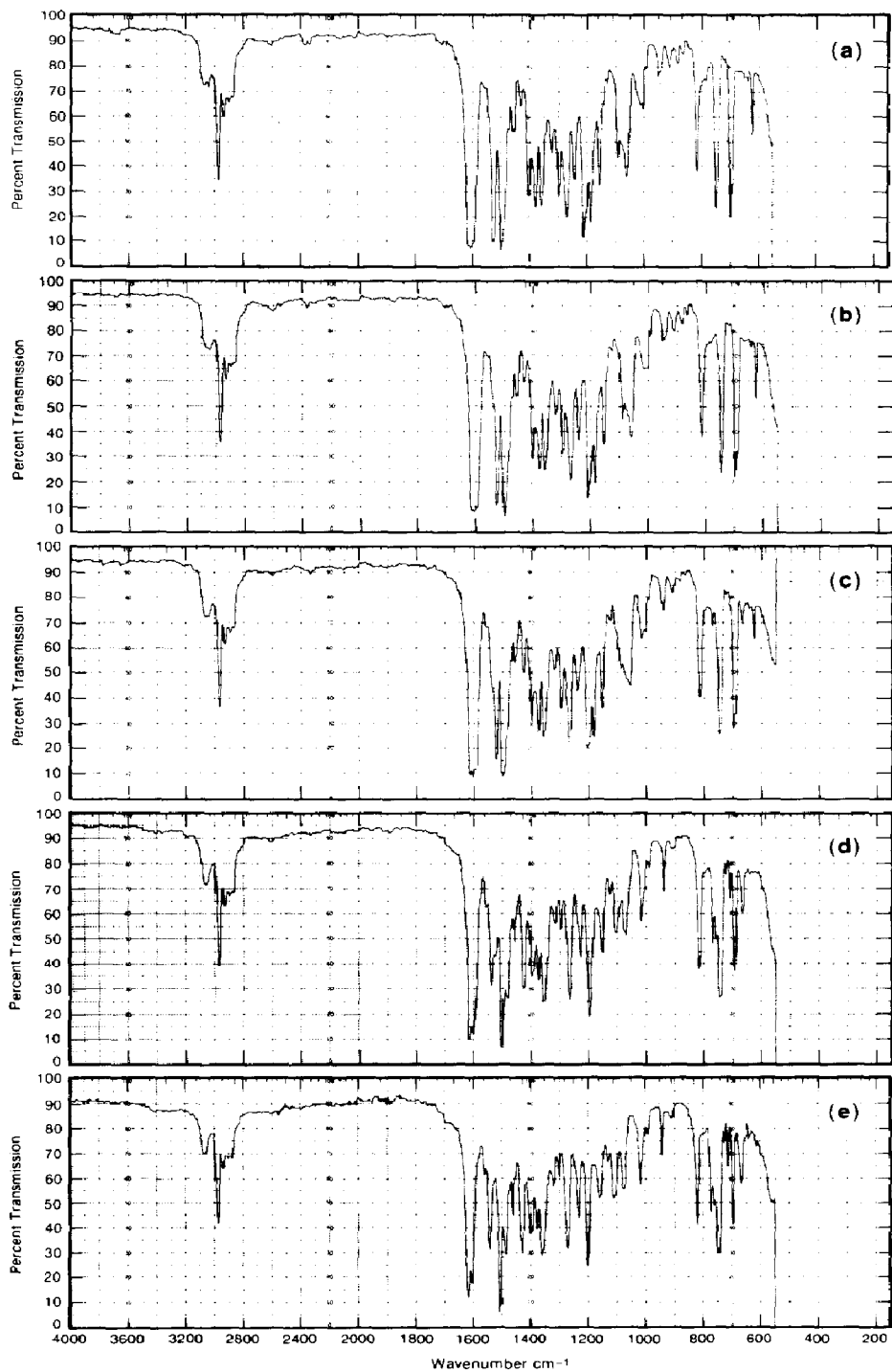
Fig. 1. The IR spectrum of 1 recorded after (a) $t = 0$, (b) $t = 20$, (c) $t = 40$, (d) $t = 100$ and (e) $t = 160$ min of exposure to UV light ($\lambda > 3400$ Å). The irradiation was conducted in air and the initial film thickness was about 10 μm.
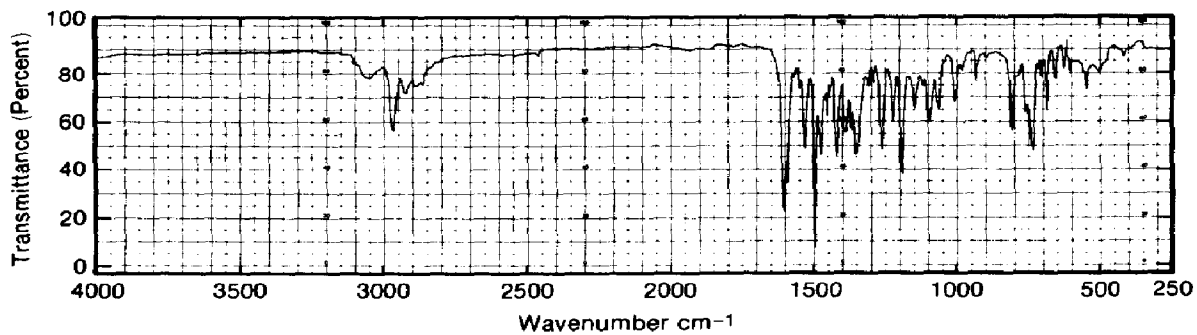
Fig. 2. The IR spectrum of a thin film of 2.
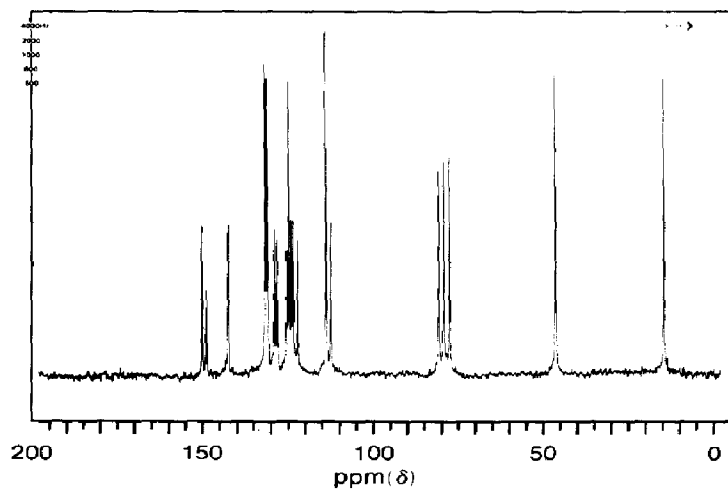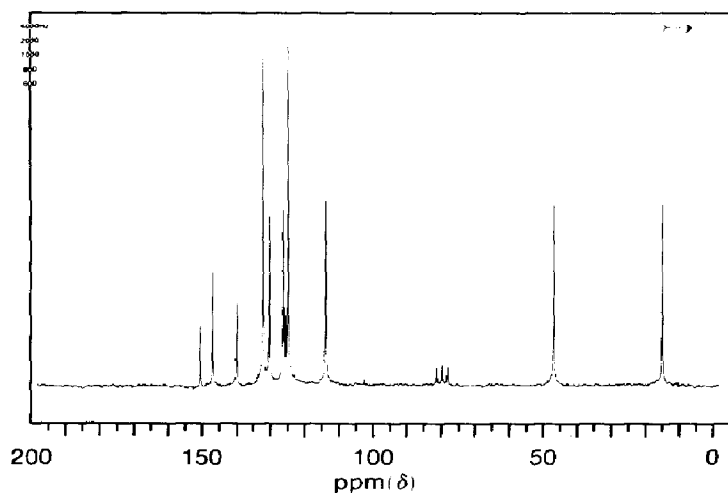
Fig. 3. C^{13} NMR (22.5 MHz, CDCl$_3$) of DEH (top) and 2 (bottom).
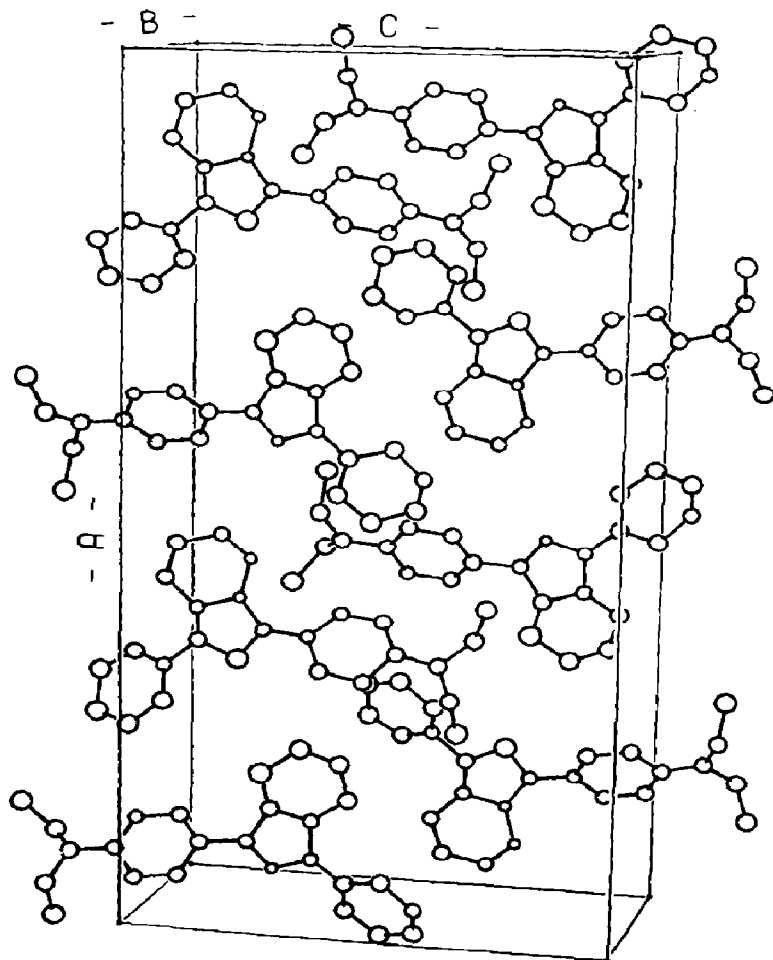
Fig. 4. The unit cell of 2 obtained by X-ray crystal structure analysis.

Photolysis of other benzaldehyde hydrazones (4) in the solid state resulted only in the recovery of starting material.
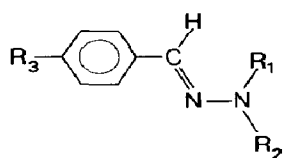
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4a	$R_1 \equiv CH_3$, $R_2 \equiv C_6H_5$, $R_3 \equiv H$
4b	$R_1 \equiv CH_3$, $R_2 \equiv C_6H_5$, $R_3 \equiv N(C_2H_5)_2$
4c	$R_1 \equiv R_2 \equiv C_6H_5$, $R_3 \equiv H$
4d	$R_1 \equiv CH_3$, $R_2 \equiv CH_2C_6H_5$, $R_3 \equiv H$
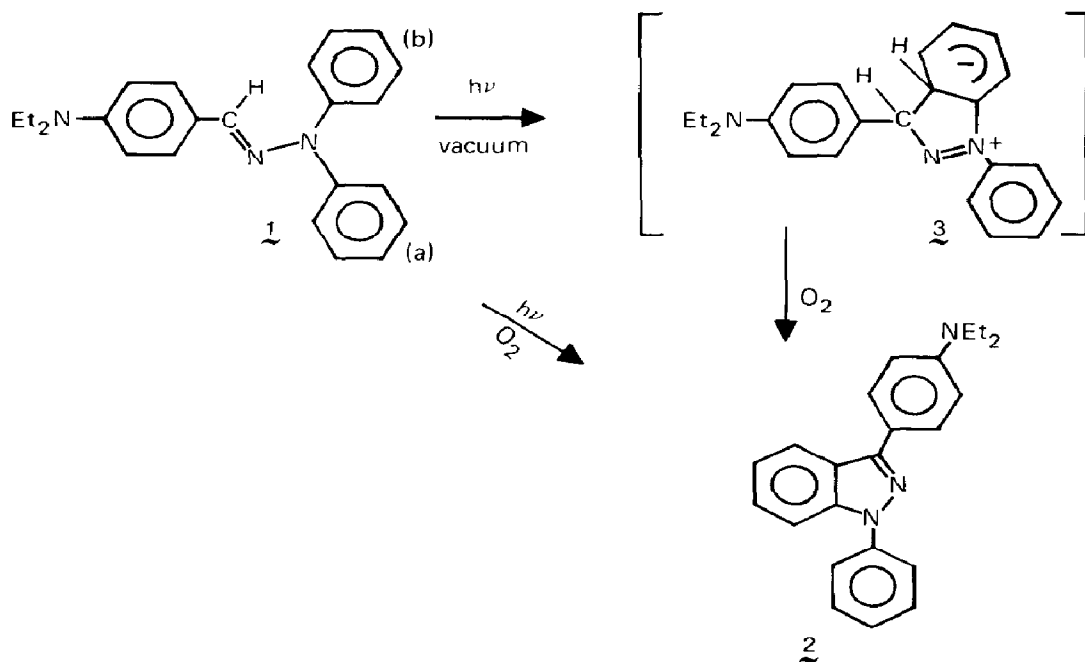
Scheme 1.

In solution aryl hydrazones have been shown to undergo homolysis of the N—N bond on photolysis to yield aryl cyanides and amines [3]. Indeed, photolysis of DEH in solution (in the presence of air) led to a variety of products, including carbazole, *p*-diethylaminobenzonitrile and diphenylamine; we could not find any spectroscopic evidence for indazole 2. Apparently the solid state prevented homolysis but only in the case of DEH was another path accessible.

Since the solid state photochemistry displayed by DEH appears to be exceptional for hydrazones, the X-ray crystal structure was solved to determine the geometry of the diphenylamine group relative to the hydrazone part of the molecule. The crystal structure of DEH (see Section 3) shows that one phenyl ring is almost coplanar with the π system while the second is nearly perpendicular to the π system. We propose that the perpendicular phenyl ring participates in the cyclization. For steric reasons, rotation of one ring requires the rotation of the second and thus there is a significant barrier to closure. Indeed, irradiation of DEH films below —20 °C resulted in no reaction.

A reasonably thorough literature search uncovered only two other examples of hydrazone photocyclizations. Yoneda and Nagamatsu [4] reported that a series of 6-(benzylidenehydrazino)-uracil derivatives underwent a cyclization followed by dehydrogenation to yield pyrazolo[3,4-α]-pyrimidines on photolysis in benzene. *o*-Nitrobenzaldehyde *N*-acylhydrazones rearranged to 1-substituted *t*-nitrophthalazines on photolysis in methanol [5].

There is ample precedent for photoreactions which involve a cyclization followed by an oxidation; the photocyclization–oxidation of stilbene to phenanthrene [6] and diphenylamine to carbazole [7] are outstanding examples. We should comment at this point that we could not detect the photoconversion of the diphenylamine part of DEH to a carbazole when thin films of DEH were irradiated.

In conclusion, we have demonstrated that photolysis of hydrazones in the solid state appears to be different from photolysis in solution under ambient conditions and have observed an unusual photocyclization of DEH to produce a substituted indazole. The indazole was stable to further irradiation as was observed for 3-alkyl-substituted indazoles [8].

3. Experimental details

3.1. Materials and apparatus

IR spectra were obtained with a Perkin–Elmer 521 spectrometer. UV spectra were recorded with a Cary 14 spectrophotometer. The low temperature equipment and vacuum system have been described in a previous report [1]. ^{1}H NMR spectra were recorded on a Varian HA-100 spectrometer and ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer. Mass spectra were obtained with an AEI-MS20 mass spectrometer. Melting points were uncorrected. Photolyses were carried out with either an EIMAC VIX-150 W xenon high pressure lamp or a 400 W Hanovia medium pressure lamp. The spectral regions of interest were isolated using Corning glass filters. The lamp was also fitted with a 10 cm water filter to remove IR radiation.

The diethylaminobenzaldehyde diphenylhydrazone was prepared using standard synthetic procedures [9] by reaction of the p-diethylaminobenzaldehyde and 1,1-diphenylhydrazone hydrochloride using ethanol as a solvent. Thin films of the hydrazone for spectroscopic analyses were prepared by spin coating from a tetrahydrofuran (THF) solution, or from a solvent with a higher boiling point such as 2-methoxyethyl acetate. The latter process gave thin glassy films which were more suitable for optical analysis and photochemical studies.

3.2. IR studies

Thin films of DEH (thickness, 5 - 10 μm) were prepared by spin coating solutions onto CsI disks. The films were irradiated either at ambient atmospheric conditions or in a vacuum system [1]. An Air Products closed-cycle refrigerator was also used in conjunction with the vacuum system to perform photochemical experiments at temperatures below the ambient temperature.

3.3. Preparation of 1-phenyl-3-(4-diethylamino-1-phenyl)-1,3-indazole (2)

Thin films of DEH were prepared by evaporating a dichloromethane solution of DEH on the inside surface of a glass test tube (outside diameter, 64 mm). A water-cooled Pyrex immersion well containing a 450 W Hanovia

lamp was placed inside the tube while the outside was surrounded by an iso-propanol bath. Irradiations were carried out for 30 min and dry ice was added to the bath during the photolysis so that the bath temperature did not exceed 35 °C. At the end of the irradiation the film was redissolved in dichloromethane. Thin-layer chromatography (silica gel, 10% ethyl acetate in hexane) showed the presence of unreacted DEH (R_f = 0.31) and one major and one minor fluorescent photoproduct (R_f^1 = 0.22 and R_f^2 = 0.01). The major photoproduct was isolated by column chromatography on silica gel using dichloromethane as eluent. It was identified as 2 on the basis of its spectral and physical properties: m.p. 81 - 81.5 °C; ^{1}H NMR (CDCl$_3$) δ 8.0 - 6.6 (m, 13H), 3.3 (q, J = 3.5 Hz, 4H), 1.2 (t, J = 3.5 Hz, 6H) ppm; ^{13}C NMR (CDCl$_3$) δ 151.84, 150.70, 144.46, 144.23, 133.35, 132.85, 130.85, 130.15, 127.32, 126.72, 125.97, 125.34, 124.21, 115.86, 114.46, 48.42, 16.66 ppm; IR (KBr) 2960, 1600, 1585, 1525, 1490, 1470, 1350, 1260, 1185, 1090, 810, 740 cm^{-1}; mass spectrum, m/e = 341; UV$_{max}$ (THF) 2575 (ϵ = 28 000), 2855 (ϵ = 23 000), 3450 (ϵ = 29 800) nm. The minor photoproduct was obtained by column chromatography followed by preparative thin-layer chromatography only as an impure oil and tentatively identified as 5 on the basis of its spectral properties: ^{1}H NMR (CDCl$_3$) δ 8.0 - 6.6 (m, 13H), 3.8 (broad s, 1H), 3.3 (g, J = 3.5 Hz, 2H) 1.35 (t, J = 3.5 Hz, 3H) ppm; IR (thin film) 3410, 2970, 1615, 1595, 1540, 1500, 1470, 820, 740 cm^{-1}.

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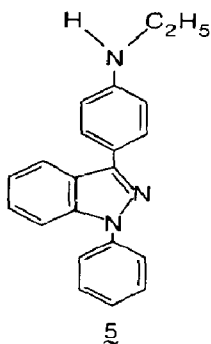
4. X-ray crystal structures

4.1. p-Diethylaminobenzaldehyde diphenylhydrazone (1)

Crystals of DEH were easily prepared using THF (distilled from LiAlH$_4$) as solvent. The yellow-colored prismatic-shaped crystals were taken for analysis and mounted in a capillary tube which was covered with a thin film of paint to keep out light.

The X-ray crystal structure analysis was performed by the Molecular Structure Corporation, College Station, Texas. Table 1 contains the pertinent crystal data for DEH. It should be noted that the crystals are triclinic with four molecules per unit cell related by a center of symmetry. However,

TABLE 1

Crystal data for DEH

Atoms	C23 H25 N3
Formula weight	343
Crystal class	Triclinic
Space group	P1̄
Lattice constants (Å)	a = 10.035(3)
	b = 10.936(2)
	c = 19.386(2)
Angles (deg)	α = 103.39(1)
	β = 93.51(1)
	γ = 99.53(1)
Z	4
V (Å^3)	2030.1(12)
d (g cm^{-1})	1.12
Radiation	Cu Kα (λ = 1.54184 Å)
$F(000)$	736
μ (cm^{-1})	5.2

the structure is somewhat unusual because there are two different molecules per unit cell. The structure for each of these is shown in Figs. 5 and 6. The salient structural features that distinguish the two systems are the relative orientations of the ethyl groups in the diethylamine portion of the molecules and the orientation of the phenyl rings in the diphenylamine portion of the molecules. In Fig. 5 the ethyl groups are oriented in a cis configuration, while in Fig. 6 they are oriented trans to each other. It should be noted that the temperature factors are somewhat large for the ethyl group containing C22 and C23 as compared with the other ethyl groups. This is most likely due to a slight disorder of this ethyl group in the crystal. A manifestation of this disorder is the rather strange values obtained for the bond lengths and angles for this particular ethyl group as shown in Tables 2 and 3. Both structures contain an extended π system from the amine nitrogen on one end of the molecule (N1 and N4) to the other amine nitrogen on the opposite end (N3 and N6). This is clearly shown in Table 4 by noting that planes labelled 1 and 4 contain the atoms forming the π system. Using the plane of the π system as a reference, the different orientations of the phenyl groups for each structure are discernible. An inspection of Tables 4 and 5 for the angles between the planes formed by the π system and the phenyl rings, and the torsional angles between selected atoms in the planes, reveals that one phenyl ring is almost planar with the π system while the other is almost perpendicular. The two structures of DEH found in the unit cell differ only slightly in the relative orientations of the phenyl rings. The structure in Fig. 6 is closer to the ideal than the structure shown in Fig. 5 because one phenyl ring is closer to coplanarity with the π system while the other is closer to being perpendicular to the π system. Figure 7 contains a description of the orientation of the two types of DEH molecules in the unit cell.

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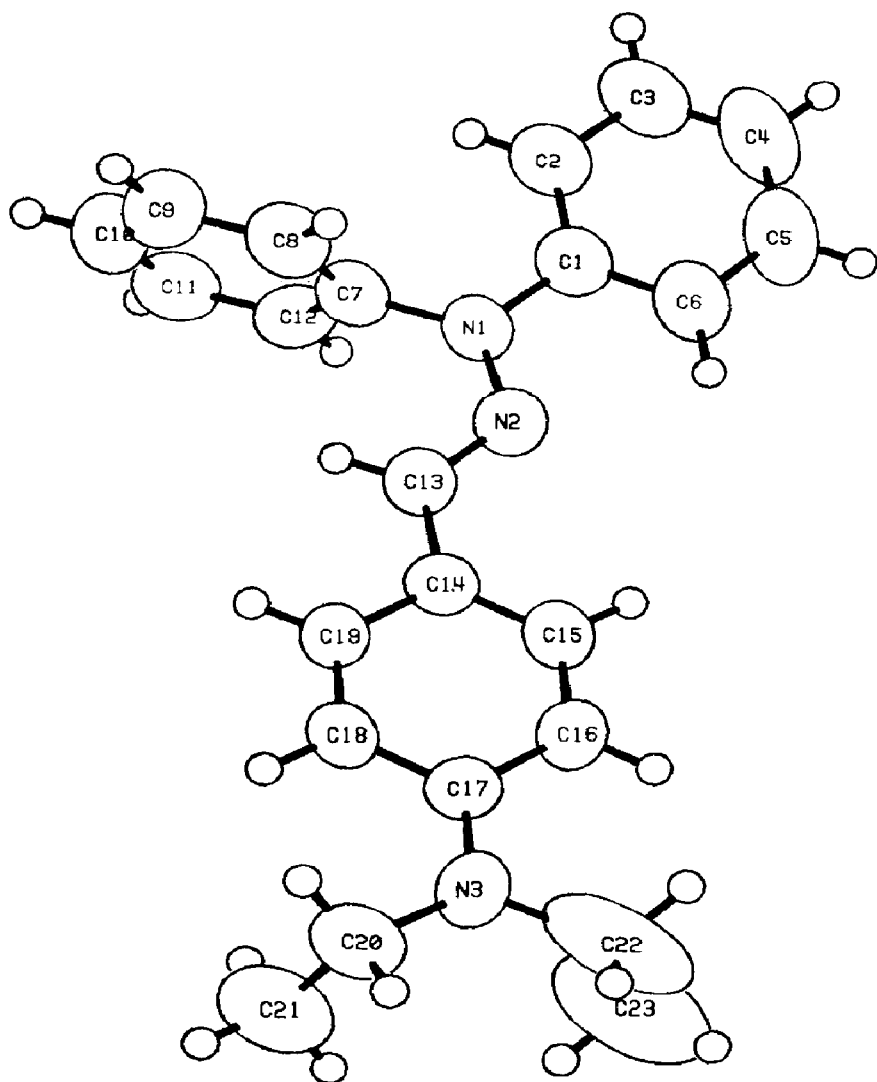
Fig. 5. The structure of 1 with the ethyl groups in a cis conformation.

In essence, both structures form an extended π system from the amine nitrogen N3 or N6 to, and including, the almost coplanar phenyl ring at the other end of the molecule. This certainly means that the lone pairs of electrons on nitrogens N1, N3 and N4, N6 are delocalized into the π system. The concomitant effect of this delocalization would be to lower the energy required for electronic excitation and removal of an electron as measured electrochemically. In addition, the crystal structure is consistent with a facile photochemical process occurring in the system by, for example, a concerted rotation of both phenyl rings coupled with bond formation between C7 and C13. This process, followed by an oxidation, could be the route for the photocyclization of DEH to an indazole in the solid state.
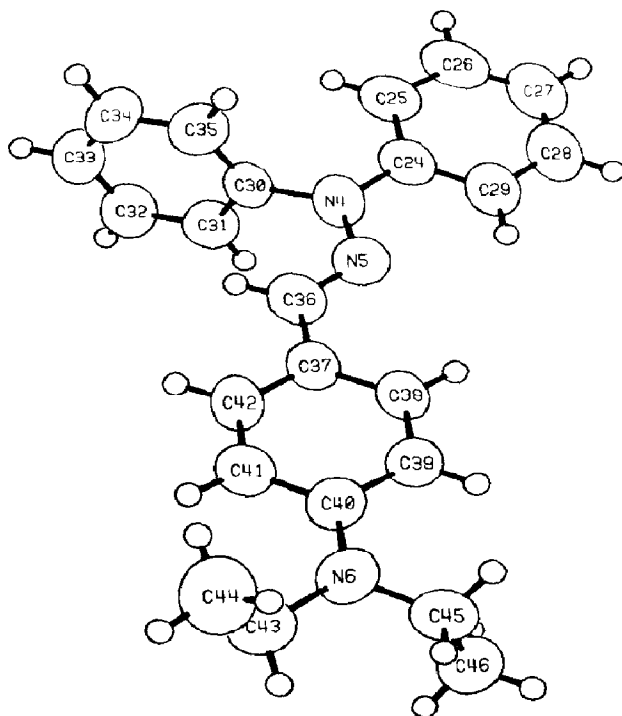
Fig. 6. The structure of 1 with the ethyl groups in a trans conformation.

TABLE 2

The bond distances in DEH (in Ångstroms)

Atom 1	Atom 2	Distance[a]	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
N1	N2	1.383(5)	C13	C14	1.459(6)	C26	C27	1.373(7)
N1	C1	1.417(6)	C14	C15	1.375(6)	C27	C28	1.356(7)
N1	C7	1.427(6)	C14	C19	1.388(5)	C28	C29	1.354(6)
N2	C13	1.287(5)	C15	C16	1.378(6)	C30	C31	1.369(6)
N3	C17	1.377(5)	C16	C17	1.403(6)	C30	C35	1.376(6)
N3	C20	1.463(6)	C17	C18	1.397(6)	C31	C32	1.357(6)
N3	C22	1.641(12)	C18	C19	1.369(6)	C32	C33	1.370(6)
C1	C2	1.368(6)	C20	C21	1.469(7)	C33	C34	1.367(6)
C1	C6	1.386(6)	C22	C23	1.189(9)	C34	C35	1.356(6)
C2	C3	1.392(6)	N4	N5	1.381(5)	C36	C37	1.449(6)
C3	C4	1.370(7)	N4	C24	1.400(5)	C37	C38	1.408(6)
C4	C5	1.353(7)	N4	C30	1.443(5)	C37	C42	1.379(6)
C5	C6	1.378(6)	N5	C36	1.278(5)	C38	C39	1.383(6)
C7	C8	1.375(6)	N6	C40	1.374(5)	C39	C40	1.396(6)
C7	C12	1.372(6)	N6	C43	1.470(6)	C40	C41	1.392(6)
C8	C9	1.378(6)	N6	C45	1.452(6)	C41	C42	1.378(6)
C9	C10	1.353(7)	C24	C25	1.385(6)	C43	C44	1.472(7)
C10	C11	1.368(7)	C24	C29	1.384(6)	C45	C46	1.493(7)
C11	C12	1.384(7)	C25	C26	1.382(6)			

[a]Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE 3

The bond angles in DEH (in degrees)

Atom 1	Atom 2	Atom 3	Angle[a]	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N2	N1	C1	116.8(4)	C13	C14	C15	125.8(5)	C26	C27	C28	119.4(6)
N2	N1	C7	122.9(4)	C13	C14	C19	116.7(5)	C27	C28	C29	121.5(6)
C1	N1	C7	119.9(4)	C15	C14	C19	117.5(4)	C24	C29	C28	120.4(5)
N1	N2	C13	116.7(4)	C14	C15	C16	121.5(4)	N4	C30	C31	119.6(5)
C17	N3	C20	122.5(5)	C15	C16	C17	120.9(5)	N4	C30	C35	120.4(5)
C17	N3	C22	122.3(5)	N3	C17	C16	122.5(5)	C31	C30	C35	120.0(5)
C20	N3	C22	112.5(5)	N3	C17	C18	120.1(5)	C31	C31	C32	119.9(5)
N1	C1	C2	120.6(5)	C16	C17	C18	117.4(5)	C31	C32	C33	120.7(5)
N1	C1	C6	119.7(5)	C17	C18	C19	120.5(4)	C32	C33	C34	118.8(5)
C2	C1	C6	119.6(5)	C14	C19	C18	122.1(4)	C33	C34	C35	121.4(5)
C1	C2	C3	120.6(5)	N3	C20	C21	112.6(5)	C30	C35	C34	119.1(5)
C2	C3	C4	119.6(5)	N3	C22	C23	99.(1)	N5	C36	C37	122.8(5)
C3	C4	C5	119.3(5)	N5	N4	C24	117.6(4)	C36	C37	C38	124.1(5)
C4	C5	C6	122.3(6)	N5	N4	C30	120.9(4)	C36	C37	C42	119.1(5)
C1	C6	C5	118.5(5)	C24	N4	C30	121.2(4)	C38	C37	C42	116.8(4)
N1	C7	C8	120.9(5)	N4	N5	C36	118.9(4)	C37	C38	C39	120.5(4)
N1	C7	C12	119.2(5)	C40	N6	C43	121.0(5)	C38	C39	C40	121.7(5)
C8	C7	C12	119.8(5)	C40	N6	C45	121.6(4)	N6	C40	C39	121.2(5)
C7	C8	C9	120.3(5)	C43	N6	C45	116.6(4)	N6	C40	C41	121.3(5)
C8	C9	C10	120.0(6)	N4	C24	C25	119.9(5)	C39	C40	C41	117.5(5)
C9	C10	C11	120.1(6)	N4	C24	C29	121.4(5)	C40	C41	C42	120.3(5)
C10	C11	C12	120.6(5)	C25	C24	C29	118.7(5)	C37	C42	C41	123.0(5)
C7	C12	C11	119.1(5)	C24	C25	C26	119.8(5)	N6	C43	C44	112.8(5)
N2	C13	C14	122.4(4)	C25	C26	C27	120.2(5)	N6	C45	C46	113.8(4)

[a]Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE 4

The weighted least-squares planes for DEH

Plane number[a]	A	B	C	D	Atom	x	y	z	Distance	Estimated standard deviation
1	0.1935	−0.9425	−0.2724	−2.7098	*Atoms in plane*					
					N1	0.8604	2.9774	−0.0428	0.082	0.004
					N2	1.4931	3.4704	−1.1700	0.046	0.004
					C13	0.7451	3.7344	−2.1830	−0.071	0.005
					C14	1.2858	4.2239	−3.4471	−0.084	0.005
					C15	2.5932	4.5816	−3.6771	−0.105	0.005
					C16	3.0223	4.9792	−4.9243	−0.057	0.006
					C17	2.1330	5.0355	−6.0075	0.013	0.005
					C18	0.8024	4.6871	−5.7653	0.018	0.005
					C19	0.4000	4.3104	−4.5123	−0.047	0.005
					N3	2.5395	5.3610	−7.2821	0.132	0.005
					Other atoms					
					C1	1.6917	2.5842	1.0355	0.319	0.005
					C7	−0.5418	2.7160	0.0072	0.043	0.005
					C20	1.6564	5.2421	−8.4428	0.389	0.006
					C22	4.1233	5.4405	−7.7041	0.478	0.008
2	0.2800	−0.8264	−0.4886	−2.1748	*Atoms in plane*					
					C1	1.6917	2.5842	1.0355	0.007	0.005
					C2	1.1924	1.8296	2.0612	−0.010	0.005
					C3	2.0064	1.4539	3.1259	0.008	0.006
					C4	3.3083	1.8799	3.1652	0.001	0.007
					C5	3.7862	2.6453	2.1566	−0.005	0.007
					C6	3.0090	3.0139	1.0794	−0.001	0.006
					Other atoms					
					N1	0.8604	2.9774	−0.0428	−0.024	0.004

(continued)

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TABLE 4 (continued)

Plane number[a]	A	B	C	D	Atom	x	y	z	Distance	Estimated standard deviation
3	−0.0916	0.4610	−0.8827	1.3016	*Atoms in plane*					
					C7	−0.5418	2.7160	0.0072	−0.006	0.005
					C8	−1.0676	1.5728	−0.5473	0.004	0.005
					C9	−2.4271	1.3479	−0.5185	−0.001	0.006
					C10	−3.2529	2.2592	0.0434	0.000	0.006
					C11	−2.7407	3.4040	0.5903	−0.002	0.005
					C12	−1.3783	3.6486	0.5674	0.006	0.005
					Other atoms					
					N1	0.8604	2.9774	−0.0428	0.030	0.004
4	−0.9837	−0.1176	−0.1357	−2.5544	*Atoms in plane*					
					N4	0.7447	7.7434	6.8960	−0.025	0.005
					N5	0.6453	7.0463	8.0838	−0.006	0.004
					C36	0.3763	7.6891	9.1557	0.038	0.005
					C37	0.2845	7.0486	10.4517	0.027	0.005
					C38	0.4338	5.6639	10.6598	0.015	0.005
					C39	0.3359	5.1298	11.9314	0.002	0.005
					C40	0.1001	5.9326	13.0490	−0.013	0.005
					C41	−0.0215	7.3041	12.8418	−0.026	0.006
					C42	0.0579	7.8252	11.5690	0.007	0.005
					N6	−0.0149	5.3885	14.3053	−0.006	0.005
					Other atoms					
					C24	1.0528	7.0145	5.7410	−0.085	0.005
					C30	0.4119	9.1456	6.8286	0.147	0.005
					C43	−0.4014	6.2166	15.4572	0.120	0.006
					C45	0.0162	3.9522	14.5179	0.103	0.006
5	−0.9735	0.0026	−0.2288	−2.3198	*Atoms in plane*					
					C24	1.0528	7.0145	5.7410	0.000	0.005
					C25	1.3290	7.6805	4.5579	0.003	0.006
					C26	1.6074	6.9594	3.4119	−0.007	0.006

(continued)

	A	B	C	D
6	0.1355	−0.0120	−0.9907	−6.8205

Atom	x	y	z		
C27	1.5822	5.5867	3.4368	0.008	0.006
C28	1.3188	4.9463	4.6024	−0.004	0.006
C29	1.0489	5.6301	5.7391	0.000	0.005
Other atoms					
N4	0.7447	7.7434	6.8960	0.037	0.005
Atoms in plane					
C30	0.4119	9.1456	6.8286	0.001	0.004
C31	−0.8910	9.5227	6.6441	0.003	0.005
C32	−1.2134	10.8400	6.5929	−0.006	0.005
C33	−0.2441	11.8023	6.7054	0.003	0.005
C34	1.0530	11.4116	6.8874	0.003	0.005
C35	1.3936	10.1005	6.9576	−0.005	0.005
Other atoms					
N4	0.7447	7.7434	6.8960	−0.003	0.004

χ^2 *values*

Plane number	χ^2
1	2164.0
2	8.0
3	4.0
4	147.0
5	4.0
6	3.0

Dihedral angles between planes

Plane number	Plane number	Dihedral angle
1	2	15.0
1	3	102.2
1	4	92.4
1	5	97.4
1	6	72.1
2	3	88.6
2	4	96.4
2	5	99.4
2	6	57.9
3	4	81.0
3	5	73.0
3	6	31.1
4	5	8.7
4	6	89.9
5	6	84.6

aThe equation of the plane is of the form $Ax + By + Cz - D = 0$ where A, B, C and D are constants and x, y and z are orthogonalized coordinates.

TABLE 5

The torsional angles in DEH (in degrees)

| Atom 1	Atom 2	Atom 3	Atom 4	Angle	Atom 1	Atom 2	Atom 3	Atom 4	Angle
C1	N1	N2	C13	175.0	C24	N4	N5	C36	179.4
C7	N1	N2	C13	2.4	C30	N4	N5	C36	−6.6
N2	N1	C1	C2	−165.9	N5	N4	C24	C25	−171.9
N2	N1	C1	C6	16.8	N5	N4	C24	C29	10.1
C7	N1	C1	C2	7.0	C30	N4	C24	C25	14.1
C7	N1	C1	C6	−170.3	C30	N4	C24	C29	−163.8
N2	N1	C7	C8	79.1	N5	N4	C30	C31	−84.8
N2	N1	C7	C12	−98.1	N5	N4	C30	C35	94.7
C1	N1	C7	C8	−93.4	C24	N4	C30	C31	88.9
C1	N1	C7	C12	89.4	C24	N4	C30	C35	−91.5
N1	N2	C13	C14	−178.2	N4	N5	C36	C37	−178.5
C20	N3	C17	C16	171.4	C43	N6	C40	C39	−173.6
C20	N3	C17	C18	−5.8	C43	N6	C40	C41	6.1
C22	N3	C17	C16	11.5	C45	N6	C40	C39	−4.1
C22	N3	C17	C18	−165.6	C45	N6	C40	C41	175.6
C17	N3	C20	C21	86.2	C40	N6	C43	C44	−86.9
C22	N3	C20	C21	−112.2	C45	N6	C43	C44	103.1
C17	N3	C22	C23	−98.9	C40	N6	C45	C46	−80.0
C20	N3	C22	C23	99.5	C43	N6	C45	C46	90.0
N1	C1	C2	C3	−179.4	N4	C24	C25	C26	−178.7
C6	C1	C2	C3	−2.1	C29	C24	C25	C26	−0.7
N1	C1	C6	C5	178.4	N4	C24	C29	C28	178.4
C2	C1	C6	C5	1.0	C25	C24	C29	C28	0.4
C1	C2	C3	C4	2.0	C24	C25	C26	C27	1.4
C2	C3	C4	C5	−0.9	C25	C26	C27	C28	−1.8
C3	C4	C5	C6	−0.2	C26	C27	C28	C29	1.5
C4	C5	C6	C1	0.1	C27	C28	C29	C24	−0.9
N1	C7	C8	C9	−178.5	N4	C30	C31	C32	179.4
C12	C7	C8	C9	−1.3	C35	C30	C31	C32	−0.2
N1	C7	C12	C11	178.7	N4	C30	C35	C34	179.9
C8	C7	C12	C11	1.5	C31	C30	C35	C34	−0.6
C7	C8	C9	C10	0.8	C30	C31	C32	C33	0.9
C8	C9	C10	C11	−0.3	C31	C32	C33	C34	−0.8
C9	C10	C11	C12	0.5	C32	C33	C34	C35	0.0
C10	C11	C12	C7	−1.1	C33	C34	C35	C30	0.7
N2	C13	C14	C15	−6.7	N5	C36	C37	C38	−2.3
N2	C13	C14	C19	172.1	N5	C36	C37	C42	176.7
C13	C14	C15	C16	177.2	C36	C37	C38	C39	179.8
C19	C14	C15	C16	−1.6	C42	C37	C38	C39	0.8
C13	C14	C19	C18	−176.5	C36	C37	C42	C41	−178.9
C15	C14	C19	C18	2.4	C38	C37	C42	C41	0.1
C14	C15	C16	C17	0.1	C37	C38	C39	C40	−0.6
C15	C16	C17	N3	−176.6	C38	C39	C40	N6	179.0
C15	C16	C17	C18	0.6	C38	C39	C40	C41	−0.6
N3	C17	C18	C19	177.4	N6	C40	C41	C42	−178.1
C16	C17	C18	C19	0.1	C39	C40	C41	C42	1.6
C17	C18	C19	C14	−1.7	C40	C41	C42	C37	−1.4
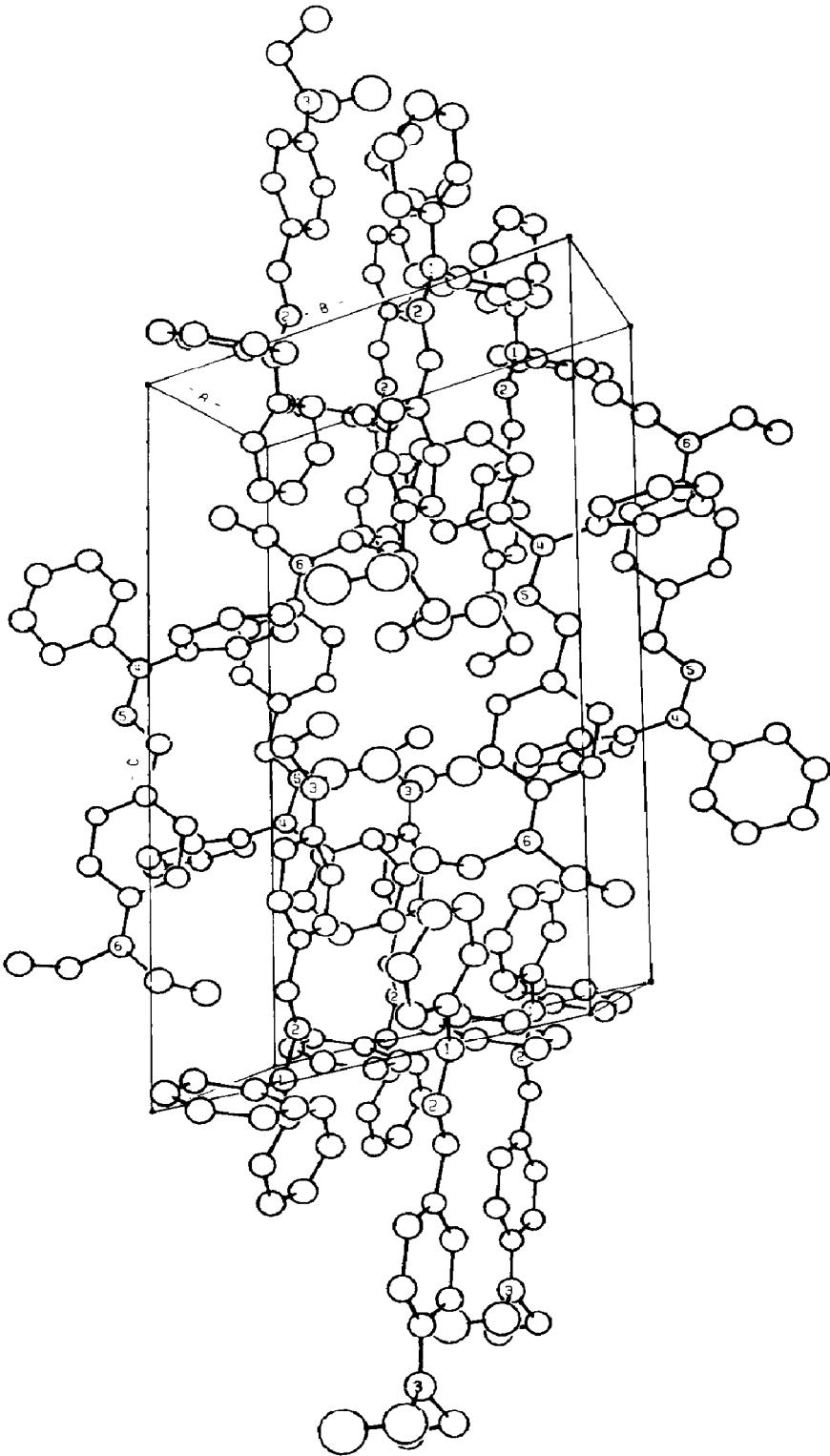
Fig. 7. The unit cell of DEH obtained by X-ray structure analysis.

The DEH crystal structure was solved by direct methods. Using 496 reflections (E_{min} = 1.99) and 2000 phase reflections, a total of 32 phase sets were produced. An E map prepared from the phase set located a total of 50 atoms with an absolute figure of merit of 0.90 and a residual of 0.43. The remaining non-hydrogen atoms were located in successive difference Fourier syntheses.

In a full least-squares refinement the function minimized was

$$\sum \omega(|F_o| - |F_c|)^2 \tag{1}$$

where the weight ω is defined as $4F_o^2/\sigma^2(F_o^2)$. The scattering factors were taken from the compilation of Cromer and Weber [10]. The values for the anomalous dispersion effects, which were also included in F_c, were taken from the values reported by Cromer and Lieberman [11]. Only the 2303 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The following values pertain to the final cycle of the least-squares refinement:

$$R_1 = \frac{\Sigma(|F_o| - |F_c|)}{\Sigma|F_o|} = 0.062 \tag{2}$$

and

$$R_2 = \left\{ \frac{\Sigma(|F_o| - |F_c|)^2}{\Sigma \omega F_o^2} \right\}^{1/2} = 0.074 \tag{3}$$

The number of observations was 2303, the number of atoms was 102 and the number of variable parameters was 469. The 50 hydrogen atoms were included in calculated positions and were not refined; the CH bond length used was 0.96 Å. The final difference Fourier map showed that the largest peaks were in the regions of the C22 and C23 ethyl groups. No other significant peaks were observed.

4.2. 1-Phenyl-3-(4-diethylamino-1-phenyl)-1,3-indazole

The X-ray crystal structure analysis was performed by the Molecular Structure Corporation, College Station, Texas. Table 6 contains the crystal data for the compound. A unit cell of the indazole contains eight molecules. However, there are two different types of molecules within the unit cell. These are shown in Figs. 8 and 9 and differ, for the most part, in the orientation of the phenyl ring in the one position with respect to the plane of the indazole ring. This may be easily seen by inspecting the position of the C9 atom in Fig. 8 and the C32 atom in Fig. 9. While the C9 atom lies below the plane of the indazole system the C32 atom lies above the plane. Since both the atoms are in the phenyl ring at the 1-position then this means that the phenyl ring is oriented differently in each case.

As noted in the introduction the motivation for obtaining an X-ray crystal structure for 2 was to identify unambiguously the structure of the material. This objective has certainly been reached but, owing to difficulties encountered growing the right crystals for analysis, a quantitative determina-

TABLE 6

Crystal data for 2

Atoms	C23 H23 N3
Formula weight	341.46
Crystal class	Orthorhombic
Space group	P NA2-1
Lattice constants (Å)	$a = 31.546(3)$
	$b = 7.781(1)$
	$c = 15.516(1)$
Z	8
V (Å^3)	3808.6(11)
d (g cm^{-3})	1.19
Radiation	Cu Kα ($\lambda = 1.54134$ Å)
F(000)	1456
μ (cm^{-1})	5.6
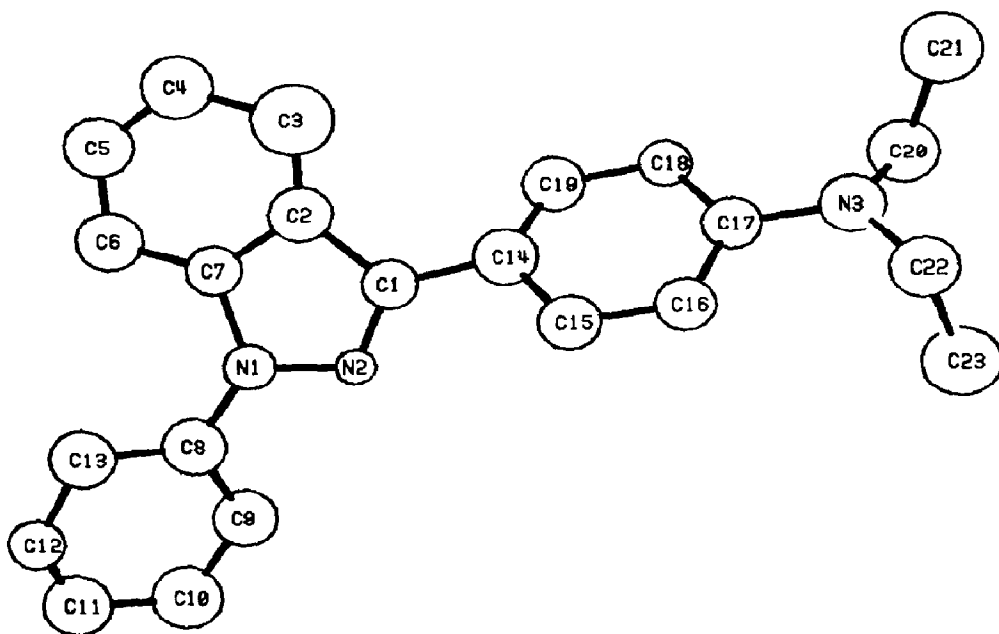
Fig. 8. One of the two structures for 2 differing as a result of rotation of the phenyl group about the N1—C8 bond.

tion of the structure for 2 could not be obtained, *i.e.* large uncertainties were encountered for some of the bond angles and lengths.

The indazole crystal structure was studied by direct methods. Using 281 reflections (E_{min} = 1.92) and 2000 phase reflections, a total of 64 phase sets were produced. An E map prepared from the phase set located a total of 46 atoms with an absolute figure of merit of 0.87 and a residual of 0.34. The remaining non-hydrogen atoms were located in successive difference Fourier syntheses.
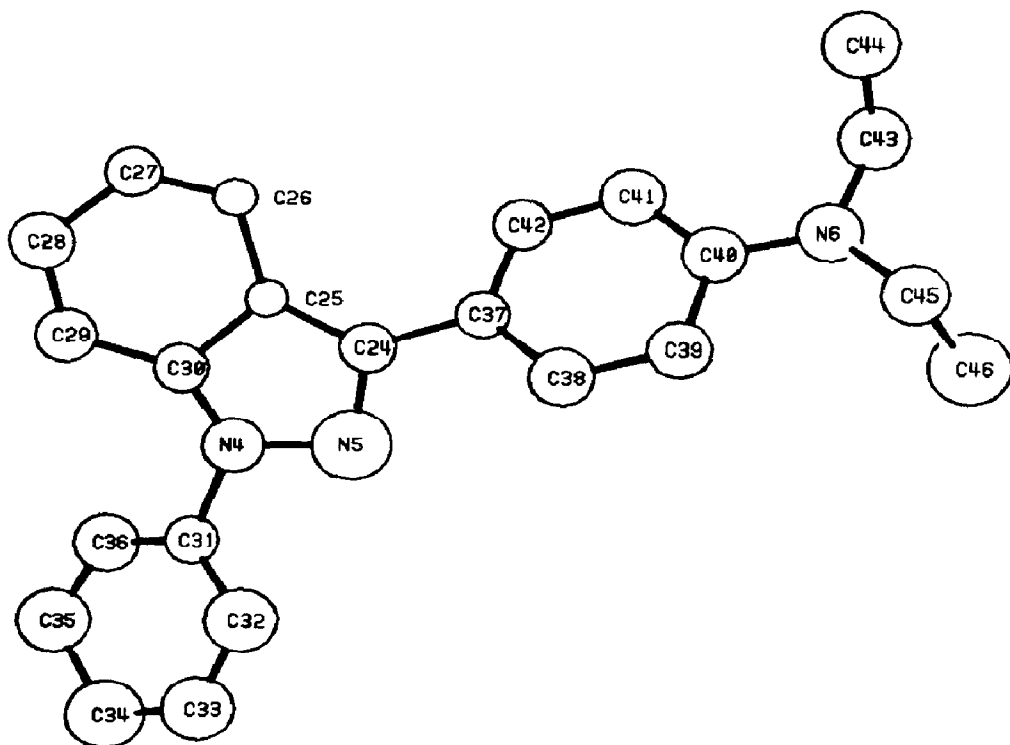
Fig. 9. One of the two structures for 2 differing as a result of rotation of the phenyl group about the N4—C31 bond.

In a full least-squares refinement the function minimized was eqn. (1). The scattering factors were taken from the compilation of Cromer and Weber [10]. The values for the anomalous dispersion effects, which were also included in F_c, were taken from the tabulation reported by Cromer and Lieberman [11]. Only the 2096 reflections having $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The following values pertain to the final cycle of the least-squares refinement: $R_1 = 0.204$ and $R_2 = 0.240$ (see eqn. (2) for the definition of R_1 and eqn. (3) for R_2). The number of observations was 2096, the number of atoms was 52 and the number of variable parameters was 208. The final Fourier map showed no significant peaks.

Reflections of the type hkl where h is odd were unusually weak. This is because the two unique molecules are nearly related by a pseudosymmetry element. Thus, if all data having odd h indices were ignored then (i) the unit cell would be half as large, (ii) the space group would be $Pn2_1a$ instead of $Pna2_1$, and (iii) the two unique molecules would be almost (but not exactly) related by a crystallographic symmetry element. This crystallographic problem manifests itself in somewhat higher than normal R factors and unexpected variations in thermal parameters, bond distances and angles. However, the basic conclusion (the identity of the molecule) is not in doubt.

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