Table 2. *Distances from the oxygen atoms of the ionophore to the water molecule compared with the corresponding distances to the sodium ion for the complexed form* (*Jones et al.*, 1973) (Å)

	H_2O	Na^+		H_2O	Na^+
O(1)	3·09	2·97	O(10)	3·02	2·85
O(2)	2·56	2·71	O(11)	2·85	2·76
O(7)	2·73	2·72	O(12)	3·16	3·12
O(8)	2·92	2·74	O(14)	3·10	3·17

Two intramolecular hydrogen bonds are observed. The double-bonded O atom of the carboxyl group, O(1), is a hydrogen-bond acceptor from both hydroxy groups O(3), 2·64 Å, and O(14), 2·99 Å. The latter is the familiar 'head to tail' hydrogen bond which serves to stabilize the overall conformation of the complex; the former hydrogen bond is a short-range one and serves to lock the carboxyl end of the molecule into a specific conformation so that the other O atom is optimally located for interaction with either the water molecule or an ion. The water molecule accepts a hydrogen bond from the carboxyl group [O(1*W*)···O(2), 2·56 Å] and donates protons to O(7), 2·73 Å, and O(11), 2·85 Å. In addition, there is also a close contact between the water molecule and O(8), 2·92 Å. The acetone molecule is not involved in any contacts of less than 3·4 Å and the closest contact between adjacent A204A molecules is 3·45 Å.

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The π-Molecular Complex Stilbene–(*sym*-Trinitrobenzene)$_2$

BY I. BAR

Chemistry Department, Ben-Gurion University of the Negev, Beersheva, Israel

AND J. BERNSTEIN*

Chemistry Department, University of Illinois, Urbana, Illinois 61801, *USA*

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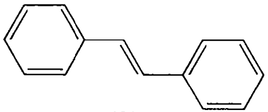
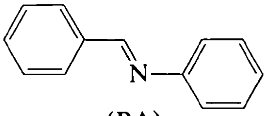
Abstract. $C_{14}H_{12}.(C_6H_3N_3O_6)_2$, triclinic, $P\bar{1}$, a = 12·407 (10), b = 7·634 (6), c = 7·421 (2) Å, α = 105·89 (5), β = 85·68 (5), γ = 92·03 (5)°, one complex per cell, D_m = 1·49, D_c = 1·493 g cm^{-3}. Yellow prismatic crystals elongated along c were grown from chloroform at 5 °C. Stacks with each phenyl ring of the stilbene sandwiched between two translationally equivalent acceptor molecules extend in the c direction; the ethylene portion of the donor appears to be uncomplexed. The stilbene molecule exhibits signs of disorder similar to that found in all previous stilbene structures.

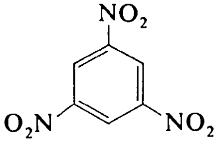
Introduction. Among the many 'additive compounds' prepared by Sudborough (1910, 1916) were the 1:2 complexes formed between the isoelectronic analogues *trans*-stilbene (S) and benzylideneaniline (BA) with trinitrobenzene (TNB).



(S)



(BA)



(TNB)

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[*] Permanent address: Chemistry Department, Ben-Gurion University of the Negev, Beersheva, Israel. Correspondence should be addressed to this author.

The first reported crystallographic investigation of either of these 'compounds' was by Hertel & Schneider (1932) who investigated the S complex, determining cell constants and proposing a possible structure (very close, in fact, to the one reported here). Although the structures of over twenty complexes with TNB acting as acceptor have been reported as of this writing, only one of them, dibenz[*a,h*]anthracene.TNB$_2$ (Zacharias, 1976) is of the ratio 1:2, and full details on that structure are not yet readily available.

The recent literature indicates a renewed interest in the precise structure of S (Hoekstra, Meertens & Vos, 1975; Bernstein, 1975; Finder, Newton & Allinger, 1974; Trætteberg, Frantsen, Mijlhoff & Hoekstra, 1975) whose crystal structure was originally determined by Robertson & Woodward (1937). S crystallizes in the $P2_1/c$ space group with two independent half molecules in the asymmetric unit, each full molecule being generated through a crystallographic center of inversion. The most precise crystal structure, studied at low temperature (Hoekstra, Meertens & Vos, 1975), proved the existence of previously suspected nonstatistical disorder about only one of these crystallographic sites. The nature of the disorder is such that it leads to an apparent shortening of the ethylenic double bond and an apparent lengthening of the exocyclic single bond (Bernstein & Mirsky, 1978). The energetic inequivalence of the two sites has been suggested by a mixed-crystal study with dibenzene mercury (Frank, Myasnikova & Kitaigorodskii, 1971), in which it was shown that the dibenzene mercury substitutes selectively at only one of the two independent crystallographic inversion centers in the S structures. Recent calculations to investigate the nature of this phenomenon (Bernstein & Mirsky, 1978) suggest that the small difference in the energetic environments of the two sites, in the order of 0·5 kcal mol^{-1}, is sufficient to account for the nonstatistical disorder at one site only.

The disorder at the one site is similar to that found in *trans*-azobenzene (Brown, 1966*a*) and in *p*-azotoluene (Brown, 1966*b*) and in one of the polymorphs of dimethylbenzylideneaniline (Bar, Bernstein & Christensen, 1976). It has also been observed in the stilbene anion complexes with Li (Walczak & Stucky, 1976). In all the structures containing S, the molecule is found at a site with point symmetry $\bar{1}$. In the hope that the environment of a charge-transfer crystal might prevent the disorder found in the earlier structures, we undertook the structure determination reported here.

Table 1. *Atomic coordinates* ($\times 10^4$ *for non-hydrogen atoms and* $\times 10^3$ *for hydrogen atoms*)

	x	*y*	*z*
C(1TN)	3325 (4)	2154 (7)	385 (7)
C(2TN)	3180 (4)	3968 (7)	1260 (8)
C(3TN)	2206 (5)	4411 (7)	2239 (8)
C(4TN)	1416 (4)	3180 (8)	2423 (8)
C(5TN)	1619 (4)	1398 (8)	1529 (7)
C(6TN)	2570 (5)	834 (8)	480 (8)
N(1TN)	4358 (4)	1596 (7)	−738 (7)
N(3TN)	2016 (5)	6360 (8)	3214 (9)
N(5TN)	770 (5)	51 (8)	1686 (8)
O(1TN)	5074 (3)	2717 (6)	−589 (7)
O(2TN)	4414 (3)	24 (6)	−1716 (6)
O(3TN)	1145 (4)	6749 (6)	4056 (9)
O(4TN)	2746 (5)	7428 (6)	3127 (10)
O(5TN)	−13 (4)	545 (8)	2713 (9)
O(6TN)	912 (5)	−1493 (7)	772 (8)
H(2TN)	374 (4)	480 (7)	124 (7)
H(4TN)	85 (4)	354 (8)	320 (8)
H(6TN)	266 (4)	−38 (8)	−14 (8)
C(1ST)	8397 (5)	6801 (10)	2901 (8)
C(2ST)	7743 (5)	8230 (9)	3931 (8)
C(3ST)	6707 (4)	7832 (9)	4504 (8)
C(4ST)	6320 (4)	6078 (8)	4200 (7)
C(5ST)	6985 (5)	4671 (9)	3143 (9)
C(6ST)	8028 (5)	5067 (9)	2575 (9)
C(7ST)	5211 (5)	5767 (8)	4958 (9)
H(1ST)	910 (4)	718 (7)	261 (7)
H(2ST)	807 (5)	940 (8)	420 (8)
H(3ST)	622 (5)	877 (8)	537 (8)
H(5ST)	679 (4)	340 (7)	286 (7)
H(6ST)	842 (4)	409 (7)	172 (7)
H(7ST)	477 (6)	691 (10)	562 (10)

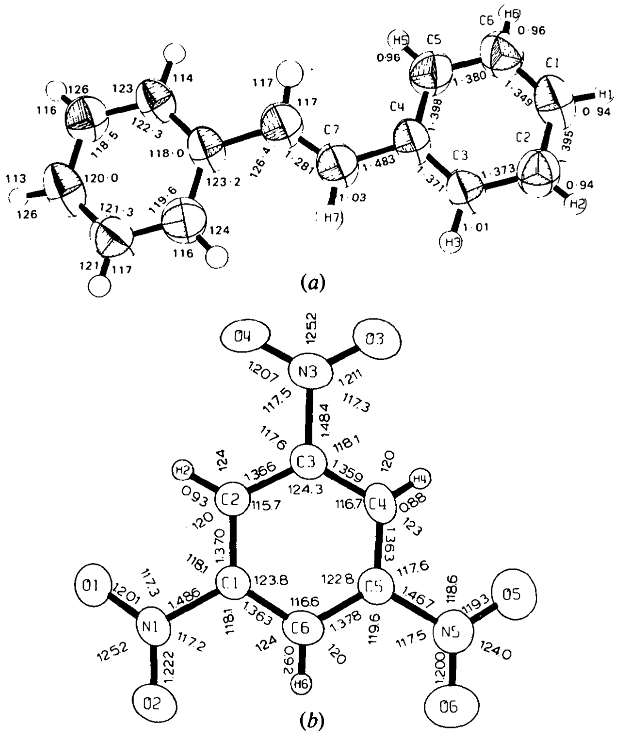

Fig. 1. Atomic numbering, bond angles (°) and bond lengths (Å) in (*a*) S and (*b*) TNB. E.s.d.'s for bond lengths involving heavy atoms are 0·009 Å except for C(7)–C(7') (0·013 Å) and for those involving hydrogen atoms (0·06 Å). E.s.d.'s for bond angles involving heavy atoms are 0·5° and for those involving hydrogen atoms 4°.

A total of 3205 reflections for $2\theta < 54{\cdot}0°$ were measured using graphite-monochromatized Mo $K\alpha$ radiation and the $\theta{:}2\theta$ scanning technique. After correction for instrumental variations and Lp factors, 1314 of the 2828 unique reflections had $I > 1{\cdot}5\sigma(I)$ and were considered observed.

The structure was solved by direct methods and refined using the *SHELX* program (Sheldrick, 1976). Anisotropic refinement on the nonhydrogen atoms and isotropic on the H atoms with half a S in one block and a whole TNB in the second block converged with $R = 0{\cdot}068$, $R_w = 0{\cdot}070$. Atomic coordinates from the final least-squares cycle are listed in Table 1.*

Discussion. Bond lengths and angles for S are given in Fig. 1(*a*). Those features of the S molecular geometry which suggested disorder in the one molecular site (Finder, Newton & Allinger, 1974; Bernstein, 1975) are present in this structure as well: C(7ST)–C(7′ST) is shorter (1·281 Å) and C(4)–C(7) longer (1·483 Å) than those found in the nondisordered molecule (1·341, 1·471 Å respectively) in the low-temperature study (Hoekstra, Meertens & Vos, 1975). As in the earlier room-temperature studies of S there is no evidence of this disorder in the final difference map, but the pattern of anisotropy of the temperature factor on C(1ST) is indicative of the same type of disorder found in one molecule in the low-temperature study (Hoekstra, Meertens & Vos, 1975) and whose energetics were studied computationally (Bernstein & Mirsky, 1978). The bond length C(1ST)–C(6ST) is somewhat shorter than the normal aromatic bond length but since the e.s.d. of this value is 0·01 Å it is only slightly more than 2σ shorter than the equivalent bond length found in the disordered molecule in earlier studies. Bond angles are quite normal and do not differ significantly from those found earlier.

The angle between the plane of the four 'bridge' atoms C(4ST)–C(7ST)–C(7′ST)–C(4′ST) and that of the six atoms in the benzene ring is 11·9°. This is considerably larger than the two values reported in the low-temperature study (Hoekstra, Meertens & Vos, 1975), 3·4 and 6·9°, but is the same as that found in the only other unsubstituted stilbene charge-transfer complex for which coordinates are available (Kodoma & Kumakura, 1974). The first authors also studied the energetics of rotation about the C–phenyl bond and suggested that the degree of rotation would be largely determined by intermolecular forces, since the potential function around a value of 0° is quite flat. Hence it appears that the energetic environment of the stilbene molecule in this crystal stabilizes a slightly less planar conformation than in the S crystal itself. However, on the basis of the estimates of Hoekstra, Meertens & Vos (1975), the increase in energy of this loss of planarity is still less than kT.

Bond lengths and bond angles for TNB are given in Fig. 1(*b*). In all cases chemically equivalent geometric features are found to be equivalent experimentally. Aromatic C–C bond lengths average 1·367 Å (e.s.d. of average 0·007 Å), a value which agrees well with that found in TNB itself (Choi & Abel, 1972). The distortion of the benzene ring from hexagonal symmetry as evidenced by the deviations of internal angles from 120° is consistent in magnitude and direction with that expected for nitro substitution (Domenicano, Vaciago & Coulson, 1975).

The planes of the nitro groups, designated by N(1TN), N(3TN) and N(5TN) make angles of 10·6, 3·1 and −6·1° with the best plane of the benzene ring, which is consistent with all the TNB molecules found in complexes to date, where none of the angles between nitro groups and the benzene ring exceeds 15°.*

The overlap between molecules and their orientation in the unit cell is given in Fig. 2. Each phenyl ring of S is sandwiched between two TNB's related to each other by a translation in the *c* direction, while the TNB above one ring of an S is related to the second below the other ring by the center of symmetry at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. The ethylenic group at the center of the S molecule is virtually in a hole in the structure, and it appears that interaction is

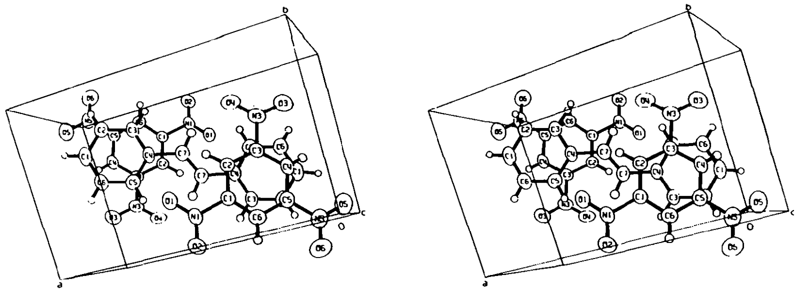

Fig. 2. Overlap diagram and disposition in the unit cell for the complex, plotted on the best plane of the four 'bridge' atoms of the S molecule. Not shown are the TNB molecules above and below the S which are related to those shown by translation in the *c* direction.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33715 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* This statement is made on the basis of a survey of all trinitrobenzene complexes for which coordinates have been checked by the Cambridge Data Center.

between the TNB's and the phenyl rings of the stilbene. In the dibenz[*a,h*]anthracene.TNB$_2$ complex the TNB molecules are also situated over the rings at the extremities of the donor molecule, and the center of the molecule is essentially uncomplexed in this structure as well (Zacharias, 1976). The distance of the TNB atoms from the 'best plane' of the S molecule varies from 3·11 Å for O(4TN) to 3·77 Å for O(2TN); the distances of the C atoms in the TNB ring are in the range 3·31 Å for C(3TN) to 3·48 Å for C(6TN). Closest interplanar atom···atom contacts are all quite normal, the shortest being C(5ST)···N(3TN) of 3·34 Å.

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(2*S*,3*R*,3a*S*,5*S*)-3a-Allyl-5-methoxy-3-methyl-2-(3′,4′-dimethoxyphenyl)-6-oxo-2,3,3a,4,5,6-hexahydrobenzofuran (a Neolignan: Porosin)

By Koychi Tomita

Instituto de Química de Araraquara, CP 174, *Araraquara, São Paulo, Brazil*

and Robert D. Rosenstein and Regina H. Almeida Santos

Instituto de Física e Química de São Carlos, São Paulo, Brazil

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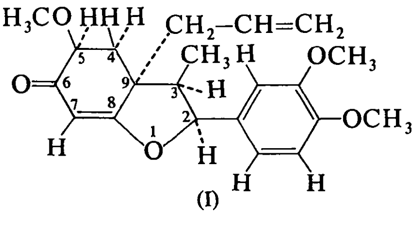
Abstract. $C_{21}H_{26}O_5$, orthorhombic, $P2_12_12$, a = 23·727 (5), b = 9·736 (5), c = 8·318 (5) Å, V = 1921·5 Å^3, Z = 4, D_c = 1·24 g cm^{-3}. The structure was solved by the direct method and Fourier difference syntheses and refined by the full-matrix least-squares method to an R value of 0·095 for 1584 observed structure amplitudes measured with Mo $K\alpha$ radiation on an automatic diffractometer.

Introduction. Porosin (I), a neolignan, was isolated from the trunk of the *Ocotea porosa* tree as part of a series of studies of natural products (Aiba, Braz Filho & Gottlieb, 1973). Two related phenyl-benzofuran neolignans have been studied by structure analysis by Tomita, Rosenstein & Jeffrey (1977) and by Tomita, Jeffrey & Shiono (1977).



(I)