Acta Cryst. (1976). B32, 718

The Crystal and Molecular Structure of a Thiocarbonyl Ylide Cycloadduct ($C_{29}H_{21}NO_2S$)

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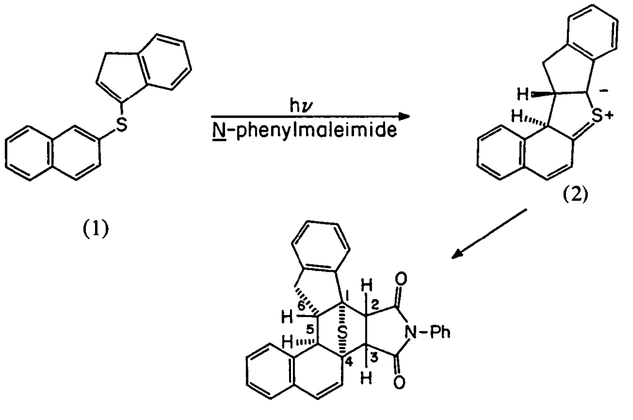
(*Received* 27 *May* 1975; *accepted* 1 *July* 1975)

1,2-Dihydronaphtho[2,1-*d*]-3*H*-indano[2,1-*f*]-*N*-phenylsuccinimido[4,3-*b*]-7α-thia-2β,3β,5α,6β-tetrahydrobicyclo[2,2,1]hepta-2,5-diene ($C_{29}H_{21}NO_2S$), an adduct resulting from addition of *N*-phenylmaleimide to a photochemically generated thiocarbonyl ylide, crystallizes in the space group $P\bar{1}$ with $a=11{\cdot}955$ (3), $b=12{\cdot}002$ (3), $c=9{\cdot}798$ (2) Å, $\alpha=75{\cdot}68$ (2), $\beta=101{\cdot}32$ (2), $\gamma=115{\cdot}32$ (1)°, $D_x=1{\cdot}32$, $D_m=1{\cdot}32$ g cm^{-3}, and $Z=2$. One benzene molecule per unit cell is located at a special position. 4998 independent diffraction intensities were recorded with Mo $K\alpha$ radiation on a four-circle diffractometer. The crystal structure was solved by application of direct methods to a selected subset of large E values. Full-matrix least-squares refinement yielded a conventional residual, $R=0{\cdot}047$. The structure determination confirms predicted stereochemical features of the molecule [Schultz & DeTar, *J. Amer. Chem. Soc.* (1974). **96**, 296–297]. All bond distances and angles are in the normal range; the average carbon bond lengths are $C(sp^2)$–$C(sp^2)=1{\cdot}393$ Å, $C(sp^2)$–$C(sp^3)=1{\cdot}510$ Å and $C(sp^3)$–$C(sp^3)=1{\cdot}548$ Å, and the average C–S bond length is $1{\cdot}848$ Å.

Recently it was reported (Schultz & DeTar, 1974) that cycloaddition of *N*-phenylmaleimide to thiocarbonyl ylide (2), photochemically generated from naphthyl vinyl sulfide (1), gave a single multicyclic adduct for which structure (3) was proposed. An understanding of the mechanism for transformation (1) → (3) required rigorous assignment of relative configuration at each of the six chiral centers generated. Herein we report a detailed account of an X-ray diffraction study of (3) which verifies the earlier structural assignment.



(1)

(3)

Experimental section

A suitable triclinic crystal was obtained from a benzene solution of a sample of (3) kindly provided by Dr A. G. Schultz. The diffraction intensities of a 0·35 × 0·30 × 0·20 mm parallelepiped crystal were measured on a Picker FACS-1 four-circle diffractometer in a θ–2θ scan mode with Zr-filtered Mo $K\alpha$ radiation. Each scan (1° min^{-1}) included a variable increment in angle above the 1·2° minimum to allow for spectral dispersion; background counts of 40 s duration were taken at both limits of each scan. Reflections within one hemisphere of reciprocal space out to $2\theta=54{\cdot}86°$ were collected. Of the 4998 independent reflections measured, 4504 were above the threshold value determined by the criterion $|F_o|\geq 1{\cdot}58\sigma_F$. The observed structure factor (F_o) and its standard deviation (σ_F) are defined as $F_o=[(C-kB)/\mathrm{Lp}]^{1/2}$, $\sigma_F=(C+k^2B)^{1/2}/(2F_o\mathrm{Lp})+0{\cdot}02F_o$. C and B represent total scan counts and background counts respectively, and k is the ratio of scan time to background count time; Lp is the Lorentz–polarization correction. In order to monitor alignment and possible deterioration of the crystal, three standard reflections were measured at intervals of 50 reflections throughout the data collection period. The standard deviation of the intensity measurement for these reflections was 1%. Lorentz–polarization and secondary extinction corrections (Zachariasen, 1968) were applied, but calculations indicated that an absorption correction was not required.

Structure determination and refinement

The structure was solved by direct methods with the program *MULTAN* (Main, Woolfson & Germain, 1971). The first attempt to determine the phases using 313 reflections with $|E|\geq 1{\cdot}5$ was not successful; the starting set selected by *MULTAN* is given in Table 1. After analyses of several E Fourier syntheses which did not contain the correct structure, we observed a possible subunit of the molecule that was periodically repeated in the E maps. It became clear that a quasi-periodicity in the local structure of the molecule could be coupling with the translational periodicity of the crystal lattice to produce a high correlation among special subsets of the E values. The sub-periodicity corresponded to a metric of about 0·1X along the x axis. Examination revealed that of the reflections with the 50 highest $|E|$ values, eight had the index $h=10$ and five others with $h=5$ corresponded to a simple multiple of this subunit metric. To reduce the dominance of these reflections in the phase determination, we removed the 16 reflections with $|E| \geq 2 \cdot 70$ (Table 2) and repeated the phase determination using the *MULTAN* program on 297 reflections. Except for the $10,\bar{3},\bar{5}$ reflection ($|E|=3 \cdot 91$) which was specified as an origin-determining reflection, the program was allowed to select the new starting set (Table 1). The E Fourier synthesis of the resulting phases contained all 33 atoms of the thiocarbonyl ylide (3). Subsequent difference Fourier synthesis revealed the existence of a benzene molecule at a center of symmetry.

Table 1. *Assignment of three origin-specifying reflections and four other reflections as a starting set for application of tangent formula*

Unsuccessful starting set					Successful starting set				
Sign	h	k	l	$\|E\|$	Sign	h	k	l	$\|E\|$
+	4	$\bar{1}$	$\bar{5}$	3·61	+	10	$\bar{3}$	$\bar{5}$	3·91
+	5	$\bar{3}$	2	3·16	+	7	$\bar{8}$	2	3·86
+	3	7	1	2·92	+	3	8	$\bar{1}$	3·55
a	8	0	2	3·99	*a*	8	0	2	3·99
b	10	$\bar{3}$	$\bar{5}$	3·91	*b*	4	$\bar{1}$	$\bar{5}$	3·61
c	3	8	$\bar{1}$	3·55	*c*	8	$\bar{3}$	$\bar{3}$	3·07
d	10	$\bar{6}$	0	3·14	*d*	1	$\bar{5}$	$\bar{8}$	2·87

Table 2. *Reflections removed from set used for phase determinations*

h	k	l	$\|E\|$	h	k	l	$\|E\|$
10	$\bar{2}$	$\bar{2}$	3·91	11	$\bar{1}$	$\bar{1}$	2·96
10	$\bar{1}$	$\bar{2}$	3·41	5	3	$\bar{6}$	2·95
9	0	1	3·37	5	1	$\bar{4}$	2·94
10	$\bar{6}$	$\bar{6}$	3·25	10	$\bar{4}$	$\bar{1}$	2·75
5	$\bar{6}$	$\bar{7}$	3·18	9	3	6	2·75
5	$\bar{3}$	2	3·16	5	$\bar{7}$	1	2·70
10	$\bar{6}$	0	3·14	10	0	$\bar{2}$	2·67
9	$\bar{1}$	1	2·96	10	0	0	2·66

After preliminary block-diagonal, least-squares refinement, the atomic coordinates and anisotropic thermal parameters were iteratively refined by a full-matrix least-squares method (Busing, Martin & Levy, 1962) using a weighting function $w=1/\sigma^2$ with $\sigma=\sum_{n=0}^{3} a_n|F_o|^n$. The coefficients, a_n, were derived from a least-squares analysis of the polynomial $||F_o|-|F_c||=\sum_{n=0}^{3} a_n|F_o|^n$. The coordinates of non-hydrogen atoms were refined in an iterative process in which anisotropic thermal parameters were used for varying subsets of the atoms until convergence was achieved. All H atoms were refined with isotropic thermal parameters. The total number of parameters thus determined was 422, including the scale factor and a secondary extinction factor (Zachariasen, 1968).

The quantity minimized in the least-squares calculations was $\sum w(|F_o|-|F_c|)^2$. Scattering factors were those of Cromer & Mann (1968) and anomalous dispersion corrections for S were those listed by Cromer (1965). The final conventional residual for 4517 reflections was $R_1=0 \cdot 047$ and the weighted residual, $R_2=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ was 0·050 with a data-to-parameter ratio of 10·7 to 1. Final parameters are in Tables 3, 4, and 5.*

Table 3. *Fractional atomic coordinates for heavy atoms* ($\times 10^4$)

Estimated standard deviations in parentheses correspond to the last significant digits (Busing, Martin & Levy, 1964).

	x	y	z
S	7779 (1)	4454 (1)	1167 (1)
O(1)	7435 (1)	2724 (1)	5205 (2)
O(2)	5085 (1)	4864 (1)	2740 (2)
N	6032 (1)	3576 (1)	4066 (2)
C(1)	8949 (2)	4875 (2)	2716 (2)
C(2)	8148 (2)	4849 (2)	3790 (2)
C(3)	7343 (2)	5560 (2)	2923 (2)
C(4)	7603 (2)	5860 (2)	1337 (2)
C(5)	8939 (2)	6875 (2)	1213 (2)
C(6)	9785 (2)	6291 (2)	2225 (2)
C(7)	10882 (2)	6281 (2)	1645 (2)
C(8)	10951 (2)	5057 (2)	2432 (2)
C(9)	11928 (2)	4683 (2)	2597 (2)
C(10)	11797 (2)	3505 (2)	3349 (2)
C(11)	10697 (2)	2696 (2)	3937 (2)
C(12)	9708 (2)	3051 (2)	3780 (2)
C(13)	9846 (2)	4244 (2)	3037 (2)
C(14)	6711 (2)	6282 (2)	269 (2)
C(15)	6923 (2)	7495 (2)	−6 (2)
C(16)	7982 (2)	8423 (2)	692 (2)
C(17)	8020 (3)	9606 (2)	714 (3)
C(18)	9024 (3)	10450 (2)	1409 (3)
C(19)	10004 (3)	10144 (2)	2076 (3)
C(20)	9994 (2)	8981 (2)	2055 (2)
C(21)	8992 (1)	8118 (1)	1375 (2)
C(22)	7222 (2)	3583 (2)	4441 (2)
C(23)	6017 (2)	4677 (2)	3182 (2)
C(24)	4920 (2)	2536 (2)	4538 (2)
C(25)	4474 (2)	1459 (2)	3990 (3)
C(26)	3394 (2)	465 (2)	4436 (3)
C(27)	2777 (2)	567 (2)	5401 (3)
C(28)	3223 (2)	1635 (2)	5941 (3)
C(29)	4310 (2)	2635 (2)	5526 (2)
C(30)	4337 (3)	8792 (3)	577 (4)
C(31)	4946 (3)	9664 (3)	1434 (3)
C(32)	5605 (3)	10865 (3)	857 (4)

Results and discussion

A perspective view of the structure of the thiocarbonyl ylide cycloadduct (3) is shown in Fig. 1 (Johnson, 1965). Bond lengths and bond angles in the molecule are indicated in Figs. 2 and 3 respectively.

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* Lists of observed and calculated structure factors, equations of least-squares planes and the distances of atoms from these planes, and an illustration of the intermolecular packing have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31247 (26 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The structure analysis completely corroborates the basic stereochemical relationships within the heteroring system that were postulated by Schultz & DeTar (1974) on the basis of spectral data and thereby supports a proposed mechanism of a complex photochemical step in a potentially important series of synthetic reactions. It also provides a rather precise, detailed description of the configuration and conformation of the molecule required for the analysis of other complex reaction intermediates.

All bond distances and angles lie within normal ranges; the average bond lengths are aromatic $C(sp^2)$–$C(sp^2) = 1{\cdot}393$ Å, $C(sp^2)$–$C(sp^3) = 1{\cdot}510$ Å and $C(sp^3)$–$C(sp^3) = 1{\cdot}548$ Å, and the average C–S bond length is 1·848 Å. The average C–O bond length is 1·206 Å. The C–H bond lengths lie in the range 0·92 to 1·01 Å with a mean value of 0·97 Å. The sequence C(4)–C(14)–C(15)–C(16) is essentially planar with a dihedral angle of only −0·2°.

Table 4. *Thermal parameters for heavy atoms*

The anisotropic thermal parameters are in the form $\exp\,[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})\times 10^{-4}]$. The isotropic equivalent of the anisotropic thermal parameters was obtained from $B=4{\cdot}0\ [V^2 \det(\beta_{ij})]^{1/3}$. The isotropic thermal parameters are in the form $\exp\,[-B \sin^2\theta/\lambda^2]$. The standard deviation for the anisotropic thermal parameters is 0·0002.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B (Å^2)
S	76	98	92	26	−3	−40	3·65
O(1)	86	95	153	39	24	19	4·52
O(2)	65	106	156	37	18	−1	4·30
N	58	73	110	19	17	−12	3·35
C(1)	56	77	82	20	3	−25	3·02
C(2)	58	74	79	20	5	−19	2·98
C(3)	59	72	89	21	8	−17	3·11
C(4)	63	87	84	24	4	−16	3·34
C(5)	64	84	84	25	15	−7	3·29
C(6)	57	79	86	19	11	−16	3·15
C(7)	70	114	114	37	25	−4	4·02
C(8)	75	115	93	45	11	−24	3·73
C(9)	85	152	110	63	16	−23	4·37
C(10)	110	157	132	85	6	−38	4·75
C(11)	123	109	145	68	0	−38	4·72
C(12)	85	92	132	37	5	−38	4·09
C(13)	71	91	92	36	1	−33	3·37
C(14)	70	132	100	36	0	−7	4·23
C(15)	88	143	122	60	16	24	4·66
C(16)	96	105	114	47	43	23	4·14
C(17)	135	119	162	75	75	43	4·94
C(18)	162	90	194	51	99	20	5·33
C(19)	133	87	175	23	65	−14	5·24
C(20)	93	84	143	23	42	−10	4·36
C(21)	79	83	103	28	37	5	3·61
C(22)	64	81	98	26	12	−15	3·40
C(23)	65	78	99	26	13	−18	3·36
C(24)	59	74	107	20	16	−6	3·38
C(25)	105	106	178	8	50	−52	5·09
C(26)	112	100	234	−4	29	−46	6·04
C(27)	85	99	225	21	51	28	5·28
C(28)	120	121	177	61	85	40	4·96
C(29)	106	88	130	44	44	3	4·26
C(30)	148	110	334	62	104	11	6·66
C(31)	184	202	180	129	37	−3	6·89
C(32)	127	168	283	56	18	−98	7·06

A rigid-body least-squares analysis (Schomaker & Trueblood, 1968) of the anisotropic thermal parameters of the C atoms of the phenyl group resulted in an average correction of 0·02 Å; the corrected bond lengths lie in the normal range of 1·37 to 1·41 Å.

The C(1)–S–C(4) bond angle of 81·2° and C–S bond lengths of 1·838 and 1·859 Å are similar to those reported for 2,5-dimethyl-2,5-*endo*-thio-1,4-dithiane (O'Connell, 1967), which has a bridging C–S–C bond angle of 86·3° and an average C–S bond length of

Table 5. *Fractional atomic coordinates* ($\times 10^3$) *and isotropic thermal parameters for the hydrogen atoms*

Estimated standard deviations in parentheses correspond to the last significant digits (Busing, Martin & Levy, 1964). The isotropic thermal parameters from least-squares refinement are in the form $\exp\,(-B \sin^2\theta/\lambda^2)$.

	x	y	z	B (Å^2)
H(C2)	867 (2)	523 (2)	457 (2)	0·6
H(C3)	752 (2)	633 (2)	322 (2)	1·0
H(C5)	911 (2)	697 (2)	25 (2)	1·0
H(C6)	1011 (2)	666 (1)	309 (2)	0·2
H(C7)	1071 (2)	628 (2)	63 (2)	2·2
H′(C7)	1165 (2)	702 (2)	176 (2)	2·0
H(C9)	1269 (2)	527 (2)	217 (2)	2·3
H(C10)	1246 (2)	323 (2)	348 (2)	2·6
H(C11)	1061 (2)	188 (2)	443 (2)	3·1
H(C12)	895 (2)	251 (2)	418 (2)	1·6
H(C14)	600 (2)	566 (2)	−17 (2)	2·8
H(C15)	636 (2)	780 (2)	−65 (2)	3·3
H(C17)	732 (2)	978 (2)	23 (3)	3·5
H(C18)	902 (2)	1128 (2)	146 (3)	4·5
H(C19)	1073 (2)	1075 (2)	258 (2)	3·3
H(C20)	1067 (2)	875 (2)	247 (2)	2·6
H(C25)	493 (2)	141 (2)	333 (3)	3·9
H(C26)	309 (3)	−27 (2)	402 (3)	6·7
H(C27)	199 (2)	−15 (2)	571 (3)	3·8
H(C28)	278 (2)	168 (2)	664 (3)	4·3
H(C29)	469 (2)	341 (2)	592 (2)	2·8
H(C30)	392 (3)	798 (3)	101 (4)	7·4
H(C31)	492 (3)	944 (3)	246 (4)	7·6
H(C32)	606 (3)	1148 (3)	144 (4)	8·7

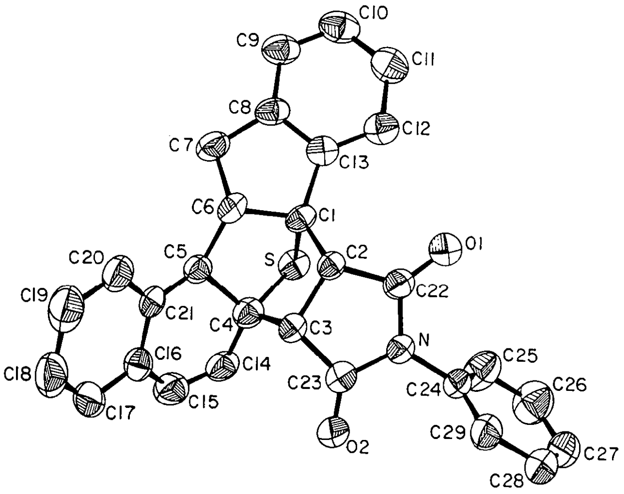

Fig. 1. A perspective view of the structure of the molecule (Johnson, 1965).

1·848 Å. The C(2)–C(1)–C(13) bond angle (124·9°) shows considerable strain; additional strain in the molecule is evidenced by the fact that all bond angles within the bicyclic ring (Fig. 3) are smaller than the unstrained tetrahedral bond angles of 109·5°. Similar strain in the base structure has been observed in a bicyclo[2,2,1]heptane system (Gopalakrishna, 1972). The bridgehead carbons [C(1) and C(4)] are located

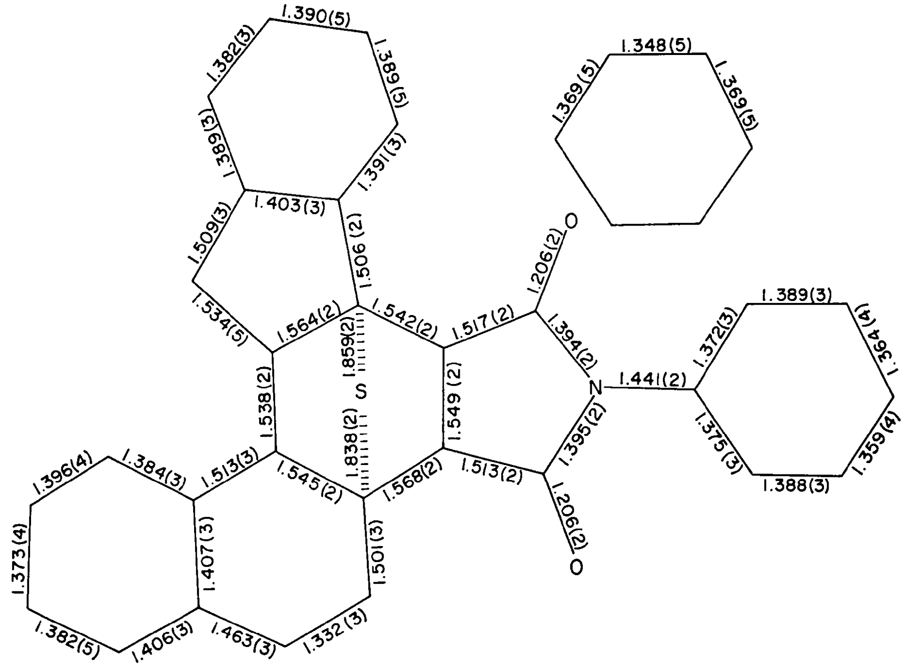

Fig. 2. Bond distances. The standard deviations are given in parentheses and refer to the last significant digit (Busing, Martin & Levy, 1964).

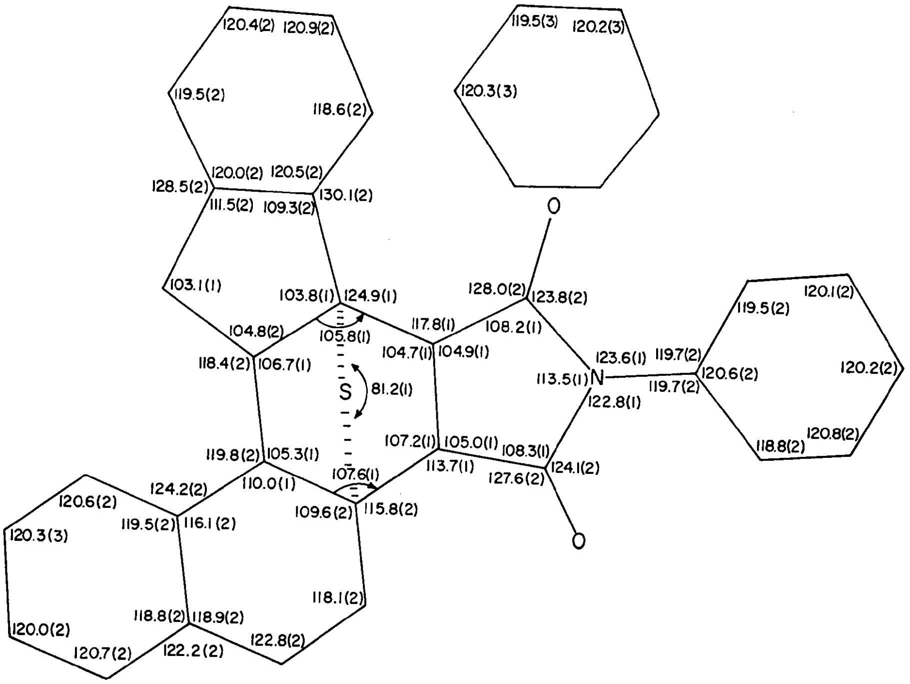

Fig. 3. Bond angles. Other angles at the bridgehead carbons C(1) and C(4) are S–C(1)–C(6), 104·0 (1); S–C(1)–C(2), 101·7 (1); S–C(1)–C(13), 114·6 (1); S–C(4)–C(5), 102·1 (1); S–C(4)–C(3), 102·4 (1); S–C(4)–C(14), 118·0 (1)°. The standard deviations are given in parentheses and refer to the last significant digit (Busing, Martin & Levy, 1964).

0·8 Å above the plane defining the bottom of the boat [C(2), C(3), C(5), C(6)], and the S atom is 2·2 Å above this plane.

Four significant sections of the molecule are very nearly planar: the phenyl group [C(24)–C(29)], the unsaturated ring of the dihydronaphthalene group [C(16)–C(21)], the six-membered ring of the indano group [C(8)–C(13)], and the succinimido group. The greatest deviation from the calculated plane was 0·023 Å for O(2) in the succinimido group. Least-squares derived equations of these planes are available.*

The four planar groups do not interact closely with any of the planar groups in other molecules. Between such parallel planes, the shortest perpendicular intermolecular distance is 3·51 Å and the shortest interatomic contact distance is 3·56 Å. The free benzene molecule at the center of symmetry is inclined at an angle of 75° to the plane of the succinimido ring and, indeed, is sharply inclined to all neighboring ring systems. The phenyl group is rotated 72° to the plane of the succinimido ring but in the opposite direction of rotation from the benzene molecule. An illustration of the intermolecular packing in the crystal structure is available.*

The shortest intermolecular non-bonded contacts are C···C (3·54 Å), C···O (3·46 Å), C···S (3·62 Å), O···H (2·67 Å), C···H (2·68 Å), H···H (2·27 Å). All of these contacts are close to the sum of the appropriate van der Waals contact distances. The intramolecular non-bonding contact O(1)···C(12) is 3·13 Å with H(C12)···O(1) distance of 2·36 Å, a relatively close interaction that is clearly driven by the rigidity of the connecting ring systems.

The authors wish to acknowledge support from the National Science Foundation through the Materials Science Center, Cornell University and the National Institutes of Health (Grant No. GM21159-02). We thank Dr A. G. Schultz for supplying the compound and for many helpful discussions. We are also grateful to Dr Victor Day for assistance in the final refinement of this structure.

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* See footnote on p. 719.