

Table 4. Bond angles (°)

Molecule (1)		Molecule (2)	
N(101)–C(101)–N(102)	115.8 (5)	N(201)–C(201)–N(202)	116.3 (5)
N(101)–C(101)–O(101)	121.1 (6)	N(201)–C(201)–O(201)	121.6 (5)
O(101)–C(101)–N(102)	123.1 (6)	O(201)–C(201)–N(202)	122.1 (5)
C(101)–N(102)–C(102)	125.8 (5)	C(201)–N(202)–C(202)	124.8 (5)
C(102)–N(102)–C(106)	118.3 (5)	C(202)–N(202)–C(206)	119.0 (5)
C(101)–N(102)–C(106)	115.8 (5)	C(201)–N(202)–C(206)	116.1 (5)
C(101)–N(101)–C(104)	123.2 (5)	C(201)–N(201)–C(204)	123.0 (5)
C(101)–N(101)–C(105)	116.1 (5)	C(201)–N(201)–C(205)	116.7 (5)
C(104)–N(101)–C(105)	120.7 (5)	C(204)–N(201)–C(205)	120.2 (5)
C(103)–C(102)–N(102)	116.0 (5)	C(203)–C(202)–N(202)	116.8 (5)
C(103)–C(102)–O(102)	126.6 (5)	C(203)–C(202)–O(202)	126.8 (5)
N(102)–C(102)–O(102)	117.4 (5)	N(202)–C(202)–O(202)	116.3 (5)
C(102)–C(103)–C(107)	122.0 (5)	C(202)–C(203)–C(207)	123.1 (5)
C(102)–C(103)–C(104)	118.5 (5)	C(202)–C(203)–C(204)	118.5 (5)
C(104)–C(103)–C(107)	119.4 (5)	C(204)–C(203)–C(207)	118.3 (5)
N(101)–C(104)–C(103)	120.2 (5)	N(201)–C(204)–C(203)	120.2 (5)
N(101)–C(104)–N(103)	117.1 (5)	N(201)–C(204)–N(203)	117.3 (5)
C(103)–C(104)–N(103)	122.7 (5)	C(203)–C(204)–N(203)	122.5 (5)
C(103)–C(107)–C(108)	122.5 (5)	C(203)–C(207)–C(208)	121.2 (5)
C(103)–C(107)–O(103)	120.4 (5)	C(203)–C(207)–O(203)	121.8 (5)
C(108)–C(107)–O(103)	117.1 (5)	C(208)–C(207)–O(203)	117.0 (5)
C(107)–C(108)–C(109)	120.7 (6)	C(207)–C(208)–C(209)	119.7 (6)
C(108)–C(109)–C(110)	127.6 (6)	C(208)–C(209)–C(210)	127.9 (6)
C(109)–C(110)–C(111)	122.9 (6)	C(209)–C(210)–C(211)	117.8 (5)
C(109)–C(110)–C(115)	118.8 (5)	C(209)–C(210)–C(215)	122.9 (5)
C(111)–C(110)–C(115)	118.2 (6)	C(211)–C(210)–C(215)	119.3 (5)
C(110)–C(111)–C(112)	120.4 (6)	C(210)–C(211)–C(212)	119.9 (6)
C(111)–C(112)–C(113)	121.3 (6)	C(211)–C(212)–C(213)	120.9 (6)
C(112)–C(113)–C(114)	118.3 (6)	C(212)–C(213)–C(214)	119.2 (6)
C(113)–C(114)–C(115)	121.9 (6)	C(213)–C(214)–C(215)	121.1 (6)
C(114)–C(115)–C(110)	119.9 (6)	C(214)–C(215)–C(210)	119.5 (6)

Table 5. Mean planes

P1: C(109), C(110), C(111), C(112), C(113), C(114), C(115)
P2: N(101), C(101), N(102), C(102), C(103), C(104)
P3: C(209), C(210), C(211), C(212), C(213), C(214), C(215)
P4: N(201), C(201), N(202), C(202), C(203), C(204)

$$P1 \wedge P2 = 5^\circ \quad P3 \wedge P4 = 6^\circ$$

$$(P_1, P_2) \wedge (P_3, P_4) = 48^\circ$$

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3,3',5,5'-Tetraiodothyroformic Acid–*N*-Diethanolamine 1:2 Salt

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Abstract. C₁₃H₆I₄O₄·2C₄H₁₁NO₂, monoclinic, *P*₂₁/*n*, *Z* = 4, *a* = 7.880 (2), *b* = 28.534 (6), *c* = 12.584 (3) Å, β = 93.16 (4)°, *M_r* = 944.08, *D_c* = 2.22 Mg m⁻³, *R* = 6.2%. Tetraiodothyroformic acid (T₄f) [3,5-diiodo-4-(4-hydroxy-3,5-diiodophenoxy)benzoic acid] forms a 1:2 salt with *N*-diethanolamine (NDEA) via a network of 13 intermolecular hydrogen-bond contacts. T₄f is a dianion with a 4'-phenoxide and 1-carboxylate anion

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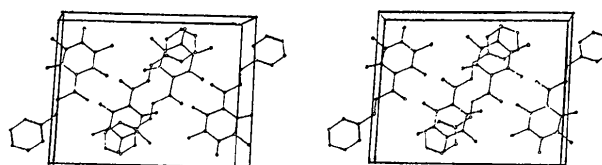


Fig. 2. Stereoview of the packing.

The X-ray analysis unambiguously demonstrates the planar structure of NSC 290115. A wide variety of planar polycyclic molecules with a high degree of activity against leukemia (Kohn, Waring, Glaubiger & Friedman, 1975; Le Pecq, Dat-Xuong, Gosse & Paoletti, 1974) have been shown to interfere with the replication of DNA through intercalation between adjacent partially unwound base pairs (Lerman, 1961). The aromatic groups of NSC 290115 are stabilized in an extended planar structure whose size fits with the base planes of the DNA. This suggests that the antitumor activity may be a consequence of an intercalative process, the affinity for the DNA being enhanced by the presence of a uracil moiety.

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geometry. The conformations of the two NDEA molecules differ; one has the extended conformation usually observed, while the other is folded. This folded NDEA also has a 50% disorder in one of its hydroxyls.

Introduction. The crystal structure determination of 3,3',5,5'-tetraiodothyroformic acid was undertaken as part of a structural study on a series (Cody, Hazel, Langs & Duax, 1977; Cody, Hazel & Osawa, 1978; Cody, 1978) of thyroxine acid metabolites. This study

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was undertaken to compare their conformational features with the naturally occurring hormones and to delineate those structural features required for their biological activity.

Crystals of T_4f (K & K Rare Chemicals, Kodak) were grown at room temperature from a methanol solution containing *N*-diethanolamine. Lattice parameters and intensities were measured on a crystal $0.04 \times 0.28 \times 0.32$ mm. The data showed the systematic absences for the space group $P2_1/n$ and the cell constants were determined by least-squares analysis of the angular settings of 64 reflections at 293 K with Mo $K\alpha$ radiation. The intensities of 6432 reflections (3297 with $I > 2\sigma$) with $2\theta < 60^\circ$ were measured on an automated diffractometer, using Zr-filtered Mo $K\alpha$ radiation, with a $2\theta-\theta$ sweep of $1.1^\circ + 0.1^\circ (\tan \theta)$. No significant changes were observed in the intensities of three standard reflections measured during data collection. A reflection was considered unobserved if the net count was less than twice the standard deviation of the background. The absorption coefficient is $\mu = 4.508 \text{ mm}^{-1}$. Intensities were corrected for Lorentz and polarization factors; however, no absorption correction was made. The I atoms were located from the Patterson map and the other nonhydrogen atoms from Fourier maps. The atomic parameters were refined by full-matrix least-squares procedures.

After three cycles of anisotropic refinement a difference Fourier map showed residual electron density consistent with a 50% disorder in the O(7) hydroxyl of one NDEA molecule. No H positions were located in the difference Fourier maps but calculated H positions were included in the refinement. This disordered model was carried throughout the subsequent refinement cycles. The weights used were the quantities $(1/\sigma_F^2)$ where σ_F is defined by Stout & Jensen (1968, equation H.14) and the instability correction was 0.06. This value increases σ_F for reflections with a large $|F|$ and prevents them from controlling the refinement. The R index, $\sum ||F_o| - |F_c|| / \sum |F_o|$, was 10.4% for 3019 reflections and the weighted R , $\sum w||F_o| - |F_c|| / \sum w|F_o|$, was 6.2%. All scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The Fourier and least-squares programs are part of the Nonius crystallographic package for the PDP 11/45 computer.

The final positions and equivalent isotropic thermal parameters are given in Table 1* and Fig. 1 shows the numbering scheme for T_4f .

Discussion. The geometry and molecular conformation of the tetraiodothyroformic acid-N-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35052 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^4$), *equivalent isotropic thermal parameters* ($\times 10^3$) and *e.s.d.'s* for the title compound

The equivalent B_{iso} are of the form: $B_{\text{iso}} = \frac{1}{3} \sum_i \sum_j B_{ij} (a_i a_j)$, taken from equation (18) of Hamilton (1959).

	<i>x</i>	<i>y</i>	<i>z</i>	B_{iso} (\AA^2)
C(1)	7384 (20)	3604 (5)	2516 (10)	30 (4)
C(2)	5734 (20)	3612 (5)	2185 (11)	34 (4)
C(3)	4981 (20)	4033 (6)	1786 (10)	32 (4)
C(4)	5856 (19)	4450 (5)	1729 (9)	27 (4)
C(5)	7650 (19)	4431 (5)	2101 (10)	28 (4)
C(6)	8345 (20)	4020 (6)	2472 (10)	38 (4)
C(7)	8288 (22)	3147 (8)	2902 (11)	41 (5)
C(1')	4268 (20)	5154 (6)	1765 (11)	38 (4)
C(2')	3581 (22)	5525 (6)	1175 (10)	37 (4)
C(3')	2661 (20)	5872 (6)	1638 (10)	31 (4)
C(4')	2313 (18)	5875 (5)	2744 (10)	23 (4)
C(5')	3054 (15)	5493 (5)	3296 (8)	18 (3)
C(6')	4025 (19)	5117 (6)	2863 (11)	36 (5)
I(3)	2513 (2)	3997 (1)	1063 (1)	55 (1)
I(5)	9154 (2)	5020 (1)	1931 (1)	57 (1)
I(3')	1699 (2)	6422 (1)	689 (1)	48 (1)
I(5')	2682 (2)	5459 (1)	4942 (1)	46 (1)
O(7)	7388 (16)	2784 (4)	2819 (9)	52 (4)
O(8)	9721 (17)	3178 (5)	3274 (12)	72 (5)
O(41)	5249 (14)	4831 (4)	1236 (7)	36 (3)
O(4'1)	1418 (13)	6192 (4)	3173 (7)	37 (3)
C(2*)	8171 (25)	1662 (6)	3162 (12)	49 (5)
C(3*)	7974 (24)	1215 (7)	2577 (14)	56 (6)
C(5*)	7356 (26)	917 (8)	781 (13)	64 (7)
C(6*)	6659 (27)	1042 (9)	-285 (14)	74 (7)
N(4*)	6901 (17)	1255 (5)	1538 (10)	44 (4)
O(1*)	9041 (14)	2001 (4)	2559 (8)	52 (3)
O(7*)	7460 (18)	1420 (7)	-664 (10)	103 (6)
C(2**)	10220 (25)	2366 (10)	-186 (16)	102 (8)
C(3**)	11091 (22)	1938 (7)	304 (13)	53 (6)
C(5**)	13011 (28)	2443 (8)	1504 (14)	65 (7)
C(6**)	14454 (23)	2518 (8)	704 (14)	58 (6)
N(4**)	12013 (19)	2018 (5)	1411 (10)	46 (4)
O(1**)	9100 (26)	2534 (8)	497 (14)	141 (8)
O(7**A)	15745 (33)	2281 (9)	1278 (20)	63 (8)
O(7**B)	15392 (31)	2055 (9)	481 (15)	53 (7)

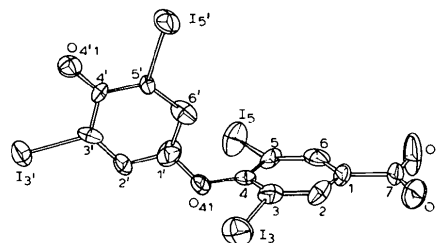


Fig. 1. Molecular conformation (50% probability thermal ellipsoids) and numbering scheme for 3,3',5,5'-tetraiodothyroformic acid.

diethanolamine 1:2 salt are illustrated in Figs. 1 and 2. The average estimated standard deviations for the nonhydrogen bond lengths and angles are 0.015 \AA and 1.0° respectively.

The shortened C–O bond lengths of the 4'-O and carboxylic group of T₄f are indicative of dianion formation, suggesting that the N of each NDEA is protonated. This type of 4'-phenoxide ion geometry (Fig. 2) was also observed in the structure of 3,3',5,5'-tetraiodothyroacetic acid (C–O = 1.31 Å) (Cody, Hazel, Langs & Duax, 1977), also an NDEA (1:1) salt; however, in the structure of the 3,3',5-triiodothyroacetic acid–NDEA 1:1 salt, the 4'-O has a normal hydroxyl geometry (C–O = 1.38 Å).

The diphenyl ether conformation, defined by the torsion angles φ [C(5)–C(4)–O(41)–C(1')] = –103 and φ' [C(4)–O(41)–C(1')–C(6')] = 7°, is skewed, as observed in other acid thyroid metabolites. This is in

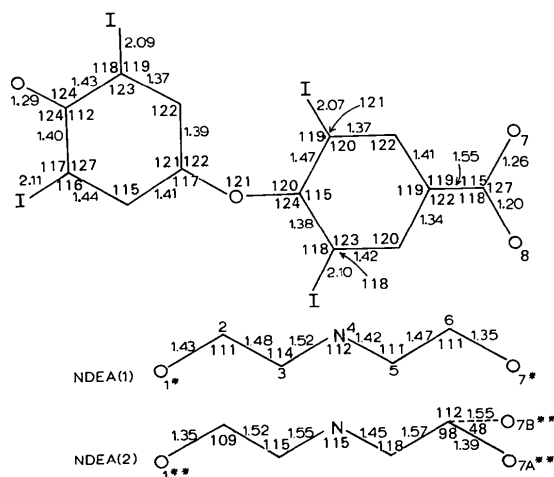


Fig. 2. Bond distances (Å) and angles (°) for the tetraiodothyroformic acid–*N*-diethanolamine 1:2 salt. O(7A) and O(7B) have a 50% disorder.

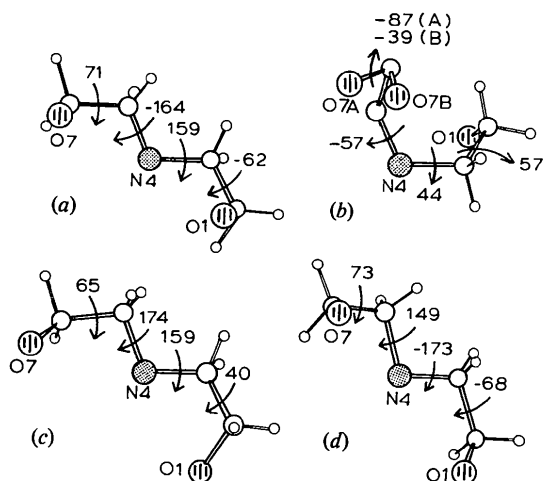


Fig. 3. Molecular conformation of *N*-diethanolamine: (a) NDEA(1), (b) NDEA(2), (c) NDEA from the triiodothyroacetic acid (1:1) salt (Cody, Hazel, Langs & Duax, 1977), (d) NDEA from the tetraiodothyroacetic acid 1:1 salt (Cody, Hazel, Langs & Duax, 1977). The average e.s.d.'s are 2.0° for each structure.

contrast to the twist-skewed conformation observed in thyronine structures (Cody, Hazel, Langs & Duax, 1977). Because the formic acid group is essentially coplanar (4°) with the inner phenyl ring, there is no distinction between a *cisoid* and a *transoid* overall conformation.

The two NDEA molecules differ significantly from one another (Figs. 2 and 3). The preferred conformation of NDEA, as observed in several structures (Cody, Hazel & Langs, 1977), appears to be a claw-shaped molecule. Molecule NDEA(2) is unusual in that it is folded, whereas NDEA(1), like the others, is extended. Molecule NDEA(2) also has a 50% disorder in the O(7) position.

As illustrated in Table 2, there are 13 intermolecular contacts less than 3.1 Å which share the eight H atoms which can participate in hydrogen bonding. The N of both NDEA molecules donates a H to the 4'-phenoxide of T₄f. These contacts of T₄f are symmetrical, from above and below the plane of the phenoxide ring, respectively.

Fig. 4 is a stereoview of the packing.

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Table 2. Intermolecular contacts less than 3.1 Å

The average e.s.d. is 0.12 Å.

†(1) O(7)···O(1*)	2.62 Å	(1) O(1*)···O(1**)	3.01 Å
(1) O(7)···O(7**A)	2.69	(1) O(1*)···N(4**)	2.82
(2) O(8)···O(7*)	2.73	(1) O(1*)···O(7**A)	2.08
(2) O(8)···O(7**B)	2.88	(1) O(7*)···O(7**B)	2.87
(4) O(4'1)···N(4*)	2.67	(1) N(4*)···O(7**A)	3.08
(4) O(4'1)···N(4**)	2.70	(1) N(4*)···O(7**B)	2.87
(1) O(1**)···O(7**A)	2.96		

† Equivalent positions: (1) x, y, z ; (2) $\bar{x}, \bar{y}, \bar{z}$; (3) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (4) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

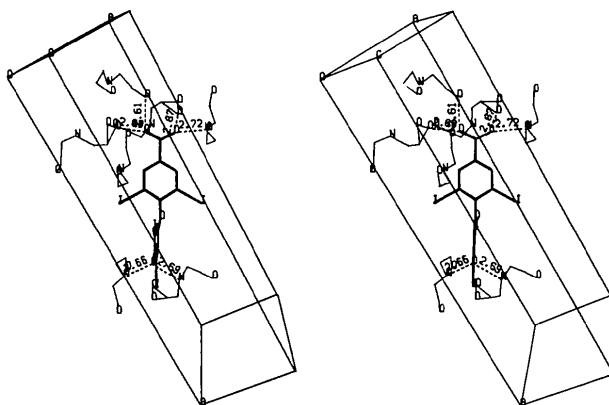


Fig. 4. Stereoview of the packing arrangement for the 1:2 salt.

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The Structure of the Charge-Transfer Complex Skatole–Tetracyanoethylene

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Abstract. $C_9H_9N.C_6N_4$, monoclinic, $C2/c$, $Z = 8$, $a = 10.07$ (1), $b = 9.97$ (1), $c = 26.45$ (2) Å, $\beta = 88.91$ (5)°, $D_x = 1.297$ (3), $D_m = 1.30$ (1) Mg m⁻³. Refinement in two blocks gave $R = 0.111$ for 1852 counter reflections with $F/\sigma(F) > 2.5$. The structure consists of two symmetry-related donor–acceptor stacks of skatole and TCNE molecules.

Introduction. Solution studies of the skatole–TCNE complex showed a well defined charge-transfer band at 550 nm (18 000 cm⁻¹). The rate of complex formation appears to be very fast, because of the immediate development of a deep-blue color.

Blue prismatic crystals were obtained from the solution by slow evaporation of the 1,2-dichloroethane solvent. When left in air at room temperature for several days, the crystals turned light brown.

Weissenberg photographs showed the systematic extinctions hkl for $h + k \neq 2n$ and $h0l$ for $l \neq 2n$. A statistical analysis of $|E_2 - 1|$ for visually estimated data indicated the space group $C2/c$. The R factor between symmetry-related structure factors (R_{sym}) was 0.24 for the visually estimated data, indicating poor crystal quality.

The intensities were collected with a Nonius CAD-4 four-circle diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å) and the $\omega/2\theta$ variable-scan method. R_{sym} was 0.14 for the best crystal available, also indicating poor crystal quality. The 1951 unique reflections measured were corrected for Lorentz and polarization

effects but not for absorption or extinction ($\mu = 0.587$ mm⁻¹). R_{sym} could not be improved by varying data-collection parameters.

The structure was solved by direct methods using *SHELX* (Sheldrick, 1975). The initial solutions showed hexagonal lattices of electron density typical of incorrect solutions of planar structures containing hexagonal rings.

E values were therefore renormalized using the equation:

$$\text{new}(E^2) = \text{old}(E^2)[0.99 - 0.03 \cos(0.32h + 0.12k + 0.017l)]$$

$$A \quad B \quad x \quad y \quad z$$

where A and B are refined by least squares, h, k, l are the Miller indices of the reflection and x, y, z are the components in fractional coordinates of a vector normal to the molecular plane (as observed in the incorrect solution) with length equal to the observed interplanar distance.

This new normalization led to a solution which showed two skatole molecules, one with much higher peaks than the other, with positions related by a non-crystallographic center of symmetry. These molecules were translated until the non-crystallographic inversion coincided with a crystallographic one. A Fourier map phased with these atomic positions showed the TCNE molecule

For refinement by least squares, the complex was divided in two blocks, one for the skatole molecule and the other for the TCNE molecule. H atoms were located using stereochemical considerations. After anisotropic refinement using weights $w = 1/[\sigma^2(F) + 0.0001F^2]$, the final R was 0.111 for the 1852 reflections with $F > 2.5\sigma(F)$ and 0.118 for all 1951

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