

C(1)—O(1)—C(8)	112.0 (5)	C(2)—O(2)—C(8)	109.4 (4)
C(3)—O(3)—C(20)	113.3 (4)	C(1)—O(4)—C(4)	108.4 (4)
C(11)—O(5)—C(12)	111.0 (4)	C(16)—O(7)—C(19)	118.2 (5)
C(12)—N(1)—C(13)	121.3 (5)	C(5)—N(1)—C(13)	123.9 (4)
C(5)—N(1)—C(12)	112.7 (4)	O(1)—C(1)—O(4)	109.0 (4)
O(4)—C(1)—C(2)	107.6 (4)	O(1)—C(1)—C(2)	105.2 (4)
O(2)—C(2)—C(1)	104.9 (4)	O(2)—C(2)—C(3)	109.8 (4)
O(3)—C(3)—C(2)	111.2 (4)	O(3)—C(3)—C(4)	109.9 (4)
O(4)—C(4)—C(3)	103.9 (4)	O(4)—C(4)—C(5)	107.8 (4)
N(1)—C(5)—C(4)	108.6 (4)	N(1)—C(5)—C(11)	99.4 (4)
N(1)—C(5)—C(6)	111.9 (4)	O(1)—C(8)—O(2)	105.6 (4)
O(2)—C(8)—C(10)	111.8 (5)	O(2)—C(8)—C(9)	108.2 (5)
O(1)—C(8)—C(10)	110.9 (4)	O(1)—C(8)—C(9)	108.2 (5)
O(5)—C(11)—C(5)	106.2 (4)	O(6)—C(12)—N(1)	127.9 (6)
O(5)—C(12)—N(1)	110.0 (5)	O(5)—C(12)—O(6)	122.0 (5)
N(1)—C(13)—C(18)	120.4 (5)	N(1)—C(13)—C(14)	122.1 (5)
O(7)—C(16)—C(15)	124.8 (5)	O(7)—C(16)—C(17)	117.0 (5)
O(3)—C(20)—C(21)	109.8 (5)		

Furanoid ring

C(1)—C(2)—C(3)—C(4)	−25.5 (5)
C(2)—C(3)—C(4)—O(4)	37.2 (5)
C(1)—O(4)—C(4)—C(3)	−36.0 (5)
C(4)—O(4)—C(1)—C(2)	19.1 (5)
O(4)—C(1)—C(2)—C(3)	5.5 (5)

Isopropylidene ring

C(8)—O(2)—C(2)—C(1)	−14.7 (5)
C(2)—O(2)—C(8)—O(1)	17.7 (6)
C(1)—O(1)—C(8)—O(2)	−13.8 (6)
C(8)—O(1)—C(1)—C(2)	4.8 (6)
O(1)—C(1)—C(2)—O(2)	6.1 (5)

Oxazolidinone ring

N(1)—C(5)—C(11)—O(5)	−5.2 (5)
C(12)—O(5)—C(11)—C(5)	8.0 (6)
C(11)—O(5)—C(12)—N(1)	−7.5 (6)
C(5)—N(1)—C(12)—O(5)	3.8 (6)
C(12)—N(1)—C(5)—C(11)	1.1 (6)

Intra- and intermolecular hydrogen-bond geometry

D—H...A	H...A	D...A	D—H...A
C(11)—H...O(3)	2.381 (7)	2.802 (7)	106.1 (5)
C(11)—H...O(4)	2.394 (8)	2.821 (8)	106.5 (5)
C(18)—H...O(6)	2.795 (8)	3.086 (8)	98.4 (5)
C(3)—H...O(6 ^b)	2.484 (6)	3.421 (6)	165.3 (5)
C(15)—H...O(4 ^b)	2.509 (7)	3.211 (7)	129.9 (5)

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 + x, y, z$.

The vinyl side chain is disordered, resulting in two sites for the terminal C(7') and C(7'') atoms with site occupancies (constrained to unity) refining to 0.65 (1) and 0.35 (1), respectively. A $\Delta\rho$ map showed the positions of all H atoms except those attached to the atoms C(6) and C(7). They were included in the refinement at calculated positions riding on their bonded atoms with fixed isotropic displacement parameters. *SHELXTL-Plus* (Sheldrick, 1991) was used for data processing, structure solution and refinement. *PARST* (Nardelli, 1983) was used for the final interpretation of molecular geometry and crystal packing. All calculations were performed on a VAX 3100 workstation.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: VJ1001). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 428–432

3,5-Dinitro-4-(4-trifluoromethylphenoxy)-toluene, Conformationally Related to Thyroid Hormones*

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(Received 9 November 1993; accepted 17 May 1994)

Abstract

The title compound, C₁₄H₉F₃N₂O₅, was synthesized as a crystalline intermediate in the synthetic route to the diiodo compound which is a potential thyroid-hormone analog. Although all the bond distances

* *Disclaimer:* This manuscript has been reviewed in accordance with the policy of the Health Effects Research Laboratory, US Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

and angles have normal values in the crystal structure, there was non-coplanarity of the nitro groups [dihedral angles between the phenyl group and N(1), O(1), O(2) and N(2), O(3), O(4) are 21.5 and 60.3°, respectively] and significant asymmetry in the bond angles at the pivotal atom, C(4), of the dinitrophenyl ring. The interplanar angle between the phenyl rings is 80.2°. Energy-refined structures for the dinitro and diiodo compounds gave interplanar angles of 80.05 and 79.65°, respectively. The skewed or twist-skewed conformation seen in thyroid hormones is reasonably well preserved in these model systems.

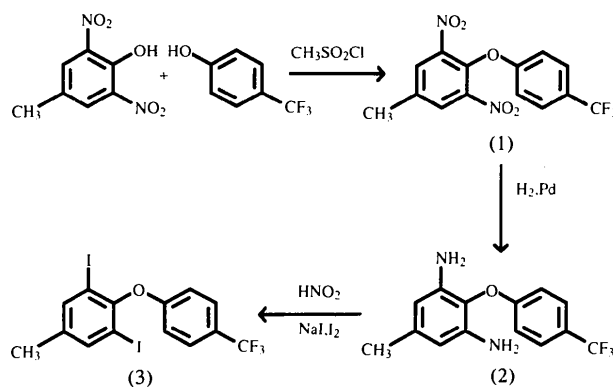
Comment

The problem of the preferred conformation of diphenyl ethers and interconversion mechanisms between stable conformers have been studied for many years using a variety of experimental techniques. A major factor in driving this research has been the structural relationship between the diphenyl ethers and thyroid hormones (Lehmann, 1972). In this respect, we have been interested (McKinney & Waller, 1994) in whether certain halogenated aromatic compounds of environmental concern, including the polychlorinated biphenyls (PCBs), diphenyl ethers, naphthalenes, dibenzofurans, and dibenzo-*p*-dioxins, exert their toxic effects through binding interactions with key proteins involved in the regulation of thyroid hormone activity. Thus, it was of interest to synthesize and characterize the structural properties and binding behavior of a diphenyl ether system related to thyroid hormones in the absence of possible complicating factors associated with the polar groups of both rings.

The title compound, (1), was synthesized as a crystalline intermediate in the synthetic route to the diiodo compound which is structurally related to thyroid hormones. It was desirable to produce a conformationally related analog of thyroid hormones in which the diiodophenyl ring would correspond to the tyrosyl ring of the thyroid hormones. The positioning of the two I atoms *ortho* to the ether O atom is important in constraining the diphenyl ether nucleus, as in thyroid hormones, to favor skewed or twist-skewed conformations (Cody, 1978). The amino acid side chain in thyroid hormones was replaced with a methyl group in the diiodo ring. It is known (Buchanan, Montaudo & Finocchiaro, 1974) that the ether O atom in thyroid hormones undergoes resonance interactions with the phenolic ring, facilitating ionization and further polarizing the tyrosyl ring. It was anticipated that substitution of a trifluoromethyl group (for the hydroxy group), corresponding to the phenolic ring, would enhance polarization of the diiodo ring system without using a polar group. The influence of such a group in

enhancing the binding of PCBs to the dioxin receptor has been demonstrated previously (Bandiera, Sawyer, Campbell, Fujita & Safe, 1983).

Condensation of 2,6-dinitro-*p*-cresol and *a,a,a*-trifluoro-*p*-cresol with methanesulfonyl chloride in pyridine according to the method of Meltzer, Lustgarten & Fischman (1957) afforded 3,5-dinitro-4-(4-trifluoromethylphenoxy)toluene (1) in 68% yield. Catalytic reduction of (1) to 3,5-diamino-4-(4-trifluoromethylphenoxy)toluene (2) was achieved smoothly using Pd on charcoal. Tetrazotization followed by treatment with sodium iodide converted (2) into the desired 3,5-diiodo-4-(4-trifluoromethylphenoxy)toluene (3) with a 61% yield. Mass spectra, proton NMR spectra, UV spectra, IR spectra, and elemental analysis (data not shown) were consistent with the assigned structures. Most characteristic in the proton NMR spectra of (1), (2) and (3) were the doublets arising from H-2' (H-6') and H-3' (H-5') with a coupling constant of 8.5–8.6 Hz. The two-proton singlet from H-3, H-5 in (1), (2) and (3) exhibited the expected chemical shifts consistent with the varying inductive effects of the *ortho* substituents.



The synthesis of the title compound is described below along with its further transformation to the diiodo derivative. Melting points were taken on a Thomas-Hoover Capillary apparatus and are uncorrected. IR spectra were determined on a Perkin-Elmer Model 1420 spectrometer as KBr pellets and UV spectra with a Beckman Model DU-70 spectrophotometer in ethanol. Proton NMR spectra were recorded on a Varian XL-400 spectrometer at 400 MHz with tetramethylsilane as the internal reference standard. Electron impact mass spectra were obtained at 70 eV by HPLC/MS using an Extrel ELQ-400-2 mass spectrometer coupled to a DuPont 8800 series HPLC *via* Extrel's Thermabeam interface. Perfluorotributylamine was used as the mass-calibration standard. Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee, USA. All reagents were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin, USA.

3,5-Dinitro-4-(4-trifluoromethoxy)toluene (1)

A solution of 2,6-dinitro-*p*-cresol (358 mg, 1.81 mmol) in pyridine (4 ml) and methanesulfonyl chloride (234 mg, 2.04 mmol) was refluxed for 10 min. After cooling to room temperature, *a,a,a*-trifluoro-*p*-cresol (864 mg, 5.3 mmol) was added and the solution refluxed for 0.5 h, then cooled and poured over ice cold water. The reaction mixture was extracted with dichloromethane, the extract washed sequentially with 4*N* HCl and water, dried over anhydrous magnesium sulfate, filtered, and concentrated by rotary evaporation. The dark brown gummy residue was chromatographed on silica gel using hexane and benzene (1:1). The eluate was crystallized from methanol-water as pale yellow plates, m.p. 367–368 K (423 mg, 68%).

3,5-Diamino-4-(4-trifluoromethylphenoxy)toluene (2)

Pd on activated charcoal (200 mg) was added to a solution of (1) (200 mg, 0.58 mmol) in ethyl acetate (100 ml) and the suspension stirred at room temperature under 20 p.s.i. (1 p.s.i. = 703.070 kg m⁻²) H₂ gas for 1.5 h. The charcoal was removed by passing through a short column of silica gel and the eluate concentrated by rotary evaporation. The residue crystallized from methanol-water as cream colored plates, m.p. 369–370 K (136 mg, 83%).

3,5-Diiodo-4-(4-trifluoromethylphenoxy)toluene (3)

Cold concentrated sulfuric acid (5 ml) was carefully added to a cooled (<273 K) stirred solution of (2) (100 mg, 0.35 mmol) in glacial acetic acid (5 ml). This solution was then added dropwise to a solution of sodium nitrite (22 mg, 3.19 mmol), acetic acid (5 ml) and sulfuric acid (5 ml), cooled to 273 K and stirred for 2 h. The reaction mixture was then added to a solution of iodine (500 mg, 1.97 mmol), sodium iodide (500 mg, 3.34 mmol), water (30 ml) and chloroform (15 ml), which had been stirred previously for 0.5 h. The whole reaction mixture was stirred for an additional 1 h. The solution was poured into a separatory funnel and the chloroform layer that separated was washed with aqueous sodium metabisulfite followed by water, subsequently dried over anhydrous magnesium sulfate, and concentrated by rotary evaporation. The dark yellow residue was chromatographed on silica gel using hexane as the eluent, which afforded needles. They were recrystallized from hexane as colorless needles (109 mg; 61%), m.p. 414–415 K.

Energy-minimized structures of the dinitro and diiodo compounds were obtained starting with the crystal structure of the dinitro compound and the general purpose Tripos 5.2 force field (Clark, Cramer & van Opdenbosch, 1989), contained within the SYBYL molecular-modeling program.

In the crystal structure of the dinitro compound (1), all the bond distances and bond angles have normal values. Thus, the mean C—C aromatic bond distance in each benzene ring is 1.383 Å. The angles at C(1) and C(4) are significantly smaller than 120° at 116.9 (3) and 116.0 (3)°, respectively. C_{ar}—CH₃ = 1.493 (6), C_{ar}—CF₃ = 1.484 (5) and C_{ar}—NO₂ = 1.473 Å. The four N—O distances in the two NO₂ groups range from 1.206 (5) to 1.217 (5) Å, with a mean of 1.211 Å. The two external bond angles at C(4) are significantly different, C(3)—C(4)—O(5) = 125.4 (3) and C(5)—C(4)—O(5) = 118.5 (3)°, which could be a result of steric repulsion between the ether O atom, O(5), and the two nitro groups. None of the nitro group planes is parallel to the plane of the benzene ring to which it is attached. The bond angle at the ether O atom, C(4)—O(5)—C(8), is 118.7 (3)°. An ORTEP (Johnson, 1965) drawing of the molecule is given in Fig. 1.

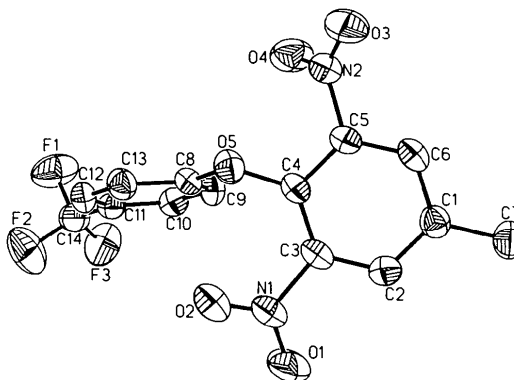
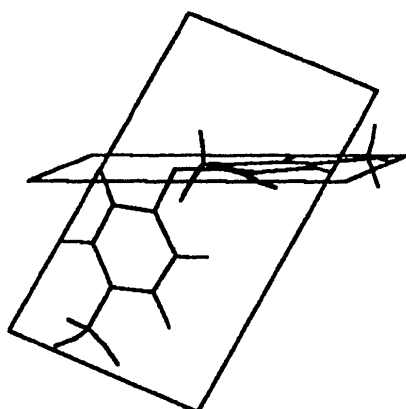


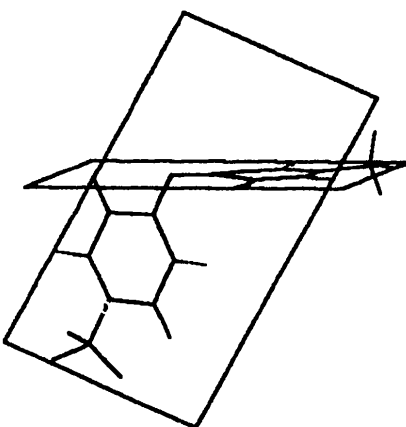
Fig. 1. An ORTEP diagram (Johnson, 1965), with 40% probability displacement ellipsoids, viewed normal to the plane of the ring containing atoms C(1)–C(6). H atoms have been omitted for clarity.

A short non-bonded intramolecular distance between the ether O atom, O(5), and a nitro group was observed: O(2)···O(5) = 2.692 Å [van der Waals radii: N(1.50 Å), O(1.40 Å) (Pauling, 1960)].

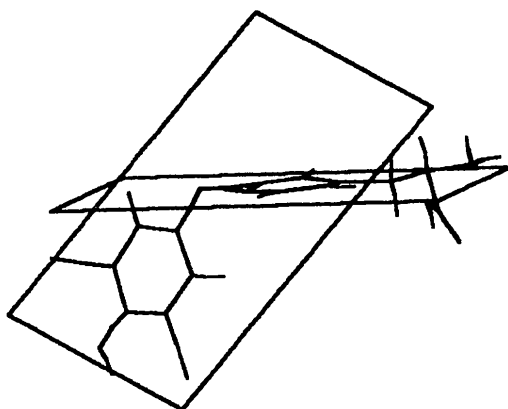
The dihedral angle between the rings in the dinitro compound is 80.2°. The energy-refined structure for the dinitro and diiodo compounds, starting with the dinitro structure and a general purpose force field, gave dihedral angles of 80.05 and 79.65°, respectively. These values compare reasonably well with the crystallographically observed angle of 94.74° for thyroxine, suggesting that the skewed or twist-skewed conformation seen in thyroid hormones is reasonably well preserved in these model compounds (Fig. 2). We have previously reported (Singh & McKinney, 1980) the structure of the less sterically constrained non-*ortho* bis(3,4-dichlorophenyl) ether as nonplanar with a dihedral angle of 73.2°.



Nitro compound
Plane angle = 80.05°



Iodo compound
Plane angle = 79.65°



T4
Plane angle = 94.74°

Fig. 2. Energy-refined structures for the dinitro (1) and diiodo (3) compounds compared to the crystal structure of thyroxine, showing plane angles.

Experimental

Crystal data

C₁₄H₉F₃N₂O₅
M_r = 342.24
Monoclinic
P2₁/c
a = 12.397 (5) Å
b = 8.277 (4) Å
c = 15.169 (6) Å
β = 109.8 (3)°
V = 1464 (1) Å³
Z = 4
D_x = 1.55 Mg m⁻³

Mo Kα radiation
λ = 0.71073 Å
Cell parameters from 15 reflections
θ = 8–10°
μ = 0.14 mm⁻¹
T = 298 K
Plate
0.50 × 0.24 × 0.20 mm
Pale yellow

Data collection

Siemens R3m/μ diffractometer
ω scans
Absorption correction: none
4059 measured reflections
3893 independent reflections
1653 observed reflections
[F_o ≥ 6σ(F_o)]

R_{int} = 0.015
θ_{max} = 29°
h = -16 → 15
k = 0 → 11
l = 0 → 20
2 standard reflections monitored every 48 reflections
intensity decay: 1.6%

Refinement

Refinement on F
R = 0.054
wR = 0.069
S = 2.0
1653 reflections
245 parameters
All H-atom parameters refined
w = 1/[σ²(F) + 0.005F²]
(Δ/σ)_{max} = 0.6

Δρ_{max} = 0.29 e Å⁻³
Δρ_{min} = -0.24 e Å⁻³
Extinction correction: Zachariasen (1963)
Extinction coefficient: 3.1 (6) × 10⁻⁶
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	U _{eq}
C(1)	0.5635 (3)	0.8982 (4)	0.1293 (2)	0.052 (1)
C(2)	0.5652 (3)	0.7310 (4)	0.1248 (2)	0.054 (1)
C(3)	0.4719 (3)	0.6381 (4)	0.1233 (2)	0.049 (1)
C(4)	0.3704 (3)	0.7086 (4)	0.1224 (2)	0.044 (1)
C(5)	0.3695 (3)	0.8754 (4)	0.1255 (2)	0.046 (1)
C(6)	0.4623 (3)	0.9693 (4)	0.1301 (2)	0.052 (1)
C(7)	0.6661 (3)	0.9976 (5)	0.1346 (3)	0.071 (2)
N(1)	0.4853 (3)	0.4623 (4)	0.1236 (2)	0.061 (1)
O(1)	0.5622 (3)	0.4085 (4)	0.0993 (3)	0.110 (2)
O(2)	0.4226 (3)	0.3782 (3)	0.1504 (2)	0.081 (1)
N(2)	0.2619 (3)	0.9574 (4)	0.1221 (2)	0.060 (1)
O(3)	0.2648 (3)	1.0441 (4)	0.1867 (2)	0.093 (2)
O(4)	0.1781 (2)	0.9342 (4)	0.0537 (2)	0.087 (1)
O(5)	0.2745 (2)	0.6259 (3)	0.1250 (2)	0.053 (1)
C(8)	0.2128 (3)	0.5324 (4)	0.0476 (2)	0.044 (1)
C(9)	0.2121 (3)	0.5646 (4)	-0.0422 (2)	0.052 (1)
C(10)	0.1500 (3)	0.4689 (4)	-0.1150 (3)	0.053 (1)
C(11)	0.0875 (3)	0.3394 (4)	-0.0990 (3)	0.050 (1)
C(12)	0.0872 (3)	0.3095 (4)	-0.0090 (3)	0.056 (2)
C(13)	0.1505 (3)	0.4072 (4)	0.0653 (2)	0.054 (1)
C(14)	0.0190 (3)	0.2368 (5)	-0.1785 (3)	0.065 (2)
F(1)	-0.0881 (2)	0.2800 (4)	-0.2147 (2)	0.114 (1)
F(2)	0.0166 (3)	0.0830 (4)	-0.1546 (2)	0.118 (1)
F(3)	0.0589 (2)	0.2343 (4)	-0.2491 (2)	0.110 (1)

Table 2. Selected geometric parameters (Å, °)

C(1)—C(2)	1.386 (5)	C(1)—C(6)	1.390 (5)
C(1)—C(7)	1.493 (6)	C(2)—C(3)	1.383 (5)
C(3)—C(4)	1.384 (5)	C(3)—N(1)	1.464 (4)
C(4)—C(5)	1.382 (4)	C(4)—O(5)	1.384 (4)
C(5)—C(6)	1.371 (5)	C(5)—N(2)	1.481 (5)
N(1)—O(1)	1.217 (5)	N(1)—O(2)	1.212 (5)
N(2)—O(3)	1.206 (5)	N(2)—O(4)	1.210 (4)
O(5)—C(8)	1.398 (4)	C(8)—C(9)	1.385 (5)
C(8)—C(13)	1.372 (5)	C(9)—C(10)	1.366 (5)
C(10)—C(11)	1.391 (5)	C(11)—C(12)	1.390 (6)
C(11)—C(14)	1.484 (5)	C(12)—C(13)	1.393 (5)
C(14)—F(1)	1.304 (4)	C(14)—F(2)	1.327 (5)
C(14)—F(3)	1.324 (6)		
C(2)—C(1)—C(6)	116.9 (3)	C(2)—C(1)—C(7)	121.7 (3)
C(6)—C(1)—C(7)	121.4 (3)	C(1)—C(2)—C(3)	122.0 (3)
C(2)—C(3)—C(4)	121.3 (3)	C(2)—C(3)—N(1)	117.3 (3)
C(4)—C(3)—N(1)	121.4 (3)	C(3)—C(4)—C(5)	116.0 (3)
C(3)—C(4)—O(5)	125.4 (3)	C(5)—C(4)—O(5)	118.5 (3)
C(4)—C(5)—C(6)	123.5 (3)	C(4)—C(5)—N(2)	118.3 (3)
C(6)—C(5)—N(2)	118.2 (3)	C(1)—C(6)—C(5)	120.3 (3)
C(3)—N(1)—O(1)	117.5 (3)	C(3)—N(1)—O(2)	119.1 (3)
O(1)—N(1)—O(2)	123.3 (3)	C(5)—N(2)—O(3)	117.8 (3)
C(5)—N(2)—O(4)	117.3 (3)	O(3)—N(2)—O(4)	124.9 (3)
C(4)—O(5)—C(8)	118.7 (3)	O(5)—C(8)—C(9)	122.6 (3)
O(5)—C(8)—C(13)	116.0 (3)	C(9)—C(8)—C(13)	121.4 (3)
C(8)—C(9)—C(10)	119.9 (4)	C(9)—C(10)—C(11)	120.0 (4)
C(10)—C(11)—C(12)	119.8 (3)	C(10)—C(11)—C(14)	119.9 (4)
C(12)—C(11)—C(14)	120.3 (3)	C(11)—C(12)—C(13)	120.2 (4)
C(8)—C(13)—C(12)	118.8 (4)	C(11)—C(14)—F(1)	114.0 (4)
C(11)—C(14)—F(2)	112.8 (3)	F(1)—C(14)—F(2)	105.3 (4)
C(11)—C(14)—F(3)	113.5 (3)	F(1)—C(14)—F(3)	105.6 (3)
F(2)—C(14)—F(3)	104.8 (4)		

Dihedral angles

Ring C(1)—C(6)/Ring C(8)—C(13)	80.2
Ring C(1)—C(6)/N(1),O(1),O(2)	21.5
Ring C(1)—C(6)/N(2),O(3),O(4)	60.3
Ring C(1)—C(6)/N(2),O(3),O(4)	76.9

All calculations were performed on a Data General Desktop Microclipse computer using *SHELXTL* (Sheldrick, 1985). The structure was solved by direct methods and Fourier techniques, and refined by blocked-cascade least-squares refinement (Sparks, 1961). A secondary-extinction correction was applied near the end of the refinement. Molecular graphics were obtained using *ORTEP* (Johnson, 1965).

We thank C. Waller and the Center for Molecular Design, Washington University, for assistance in obtaining the energy-refined structures. The technical support of Mantech Environmental Technology Inc. is acknowledged.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: CR1115). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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***N,N*-Diethyl-4-(2-nitroethenyl)phenylamine
(DEANST), C₁₂H₆N₂O₂**

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(Received 19 November 1993; accepted 26 May 1994)

Abstract

The two independent molecules *A* and *B* in the unit cell of the title compound are nearly planar except for the methyl groups at the ends of the ethyl chains. In molecule *A*, these groups are on opposite sides of the plane. In molecule *B*, one of the ethyl branches is disordered and its methyl group is either on the same (occupancy 60%) or opposite (occupancy 40%) side of the plane as the methyl group of the other branch.

Comment

DEANST, (I), is a third-order non-linear optical material (Kurihara *et al.*, 1991) whose optical properties are being studied in our laboratory. The two independent molecules have nearly the same orientation, the axes along their lengths being approximately parallel to the [111] crystallographic axis. The mean planes through the rings of the two molecules make an angle of 60 (1)°. These structural results are in full agreement with the anisotropy of the third-harmonic susceptibility (Kurihara *et al.*, 1991).