J. Org. Chem. **1995**, *60*, 4644−4646

Novel [4 + 2] Cycloadditions of Vinyltetrathiafulvalene Derivatives

Peter J. Skabara, Martin R. Bryce,*
Andrei S. Batsanov,[†] and Judith A. K. Howard

*Department of Chemistry, University of Durham,
Durham DH1 3LE, U.K.*

Received January 14, 1995

Extensive studies on tetrathiafulvalene (TTF) and its derivatives have been conducted during the past twenty years[1] because these electron donor molecules are components of charge-transfer complexes (*e.g.* TTF-TCNQ) and ion radical salts, many of which are organic metals.[2] Recently, synthetic methodology based upon lithiation of TTF[3] has been improved considerably to allow access for the first time to a wide range of monofunctionalized TTF derivatives in synthetically useful quantities,[4] and we are investigating their chemistry. In this note we describe the first examples of [4 + 2] cycloadditions to a TTF derivative in which the TTF moiety acts as a diene.[5]

Vinyltetrathiafulvalene derivatives **2a−e** were prepared in high yields by reaction of TTF-carboxaldehyde **1** with the appropriate Wittig salt (Scheme 1). For derivatives **2b−e** the *trans* isomer predominated over the *cis* isomer (^{1}H NMR analysis of the crude reaction mixture) and the former was easily purified by fractional crystallization (except for derivative **2b** which could not be separated from a small amount of the *cis* isomer). We discovered, by serendipity, the ability of these vinyl-TTF derivatives to act as dienes in the Diels−Alder reaction. With the intention of preparing a charge-transfer complex between derivative **2e** and tetracyanoethylene (TCNE), an equimolar amount of the two reactants was mixed in acetonitrile (reflux, 5 min) to afford a yellow crystalline 1:1 adduct in 68% yield upon cooling. It was immediately apparent from NMR, IR, and mass spectroscopic data that this product was not a charge-transfer complex, but a covalent compound instead! X-ray structural analysis showed the product to be the Diels−Alder adduct **3e** which had crystallized as a 1:1 acetonitrile solvate (Figure 1). A remarkable feature of the structure of adduct **3e** is that the π-bonding of TTF has been disrupted. Thus while ring A preserves the usual geometry of TTF, with a slight folding of 5.3° along the S(3)−S(4) line, ring B contains an sp^3 carbon atom, C(14), and adopts a nonsymmetric half-chair conformation. The fused six-membered ring adopts a twisted sofa conformation, with C(12) and C(13) deviating by 0.16 and −0.61 Å from the C(14)−C(15)−C(16)−C(11) plane. Compounds **2a−d** react analogously with TCNE in refluxing toluene to afford adducts **3a−d** (42−70% yield). Predictably, the reactions occur most readily when the substituent R is electron releasing, *i.e.* derivatives **2d** and **2e**.

We have briefly explored the scope of this Diels−Alder reaction by using the dienophiles *N*-phenyl-1,2,4-triazoline-3,5-dione (NPTD) and dimethylacetylene dicarboxylate (DMAD). Dienes **2a−e** reacted with NPDT to yield 1:1 adducts (mass spectrometric evidence) alongside other reaction products (TLC evidence) and only species **4d** and **4e**, obtained from the more reactive dienes, could be obtained pure (61 and 33% yields, respectively). The reaction of dienes **2a−e** with DMAD yielded complex product mixtures (TLC evidence) which contained the expected 1:1 adducts (mass spectrometric data). However, the only product isolated pure was Diels−Alder adduct **5a** (46%).

These prototype reactions of vinyl-TTF derivatives are potentially very versatile, offering scope for modification of both the diene and dienophile. An appealing consequence of the Diels−Alder reaction is that by this methodology (electron-rich diene; electron-deficient dienophile) vinyl-TTF derivatives may provide entry into covalently-linked donor-σ-acceptor systems which are candidates for molecular rectifiers.[6]

Experimental Section

General. Details of instrumentation are the same as those reported recently.[7] All reactions were carried out using dried distilled solvents under a dry nitrogen atmosphere.

Preparation of Compounds 2a−e. General Procedure. To a suspension of the respective Wittig salt in tetrahydrofuran (THF) (60 mL) was added butyllithium (1.6 M in hexane) at −78 °C. The reaction was stirred at this temperature for 15 min whence TTF-carboxaldehyde (**1**)[4c] was added and the reaction temperature raised to 20 °C, with stirring for a further 16 h. The reaction mixture was evaporated under reduced pressure and the residue extracted into dichloromethane. Water was added, and the organic layer was separated, dried (MgSO$_4$), and evaporated. Purification by column chromatography using silica gel and toluene as the eluent afforded the product, which was recrystallized from dichloromethane−hexane where applicable.

1-[2,2′-Bi(1,3-dithiolylidene)-4-yl]ethylene (2a): orange oil (80% yield) following the literature procedure.[8]

[†] On leave from the Nesmeyanov Institute of Organoelement Compounds, Moscow, Russia.

[1] For initial references to TTF see: (a) F. Wudl, F.; Smith, G. M.; Hufnagel, E. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1453. (b) Hünig, S.; Kiesslich, G.; Scheutzow, D.; Zahradnik, R.; Carsky, P. *Int. J. Sulfur Chem. Part C* **1971**, 109. (c) Ferraris, J.; Cowan, D. O.; Walatka, V. V.; and Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948.

[2] For recent reviews on TTF chemistry see: (a) Krief, A. *Tetrahedron* **1986**, *42*, 1209. (b) Bryce, M. R. *Chem. Soc. Rev.* **1991**, *20*, 355. (c) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors (Including Fullerenes);* Prentice Hall: New Jersey, 1992. (d) Hansen T. K.; Becher, J. *Adv. Mater.* **1993**, *5*, 288.

[3] (a) Green, D. C.; Allen, R. W. *J. Chem. Soc., Chem. Commun.* **1978**, 832. (b) Green, D. C. *J. Org.Chem.* **1979**, *44*, 1476.

[4] (a) Moore, A. J.; Bryce, M. R. *J. Chem. Soc., Chem. Commun.* **1991**, 1638. (b) Moore, A. J.; Skabara, P. J.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K.; Daley, S. T. A. K. *J. Chem. Soc. Chem. Commun.* **1993**, 417. (c) Garín, J.; Orduna, J.; Uriel, S.; Moore, A. J.; Bryce, M. R.; Wegener, S.; Yufit, D. S.; Howard, J. A. K. *Synthesis* **1994**, 489.

[5] Recently, the first two examples of TTF acting as a 2π electron dienophile have been reported. For a remarkable reaction of the central C═C bond of TTF see: Hopf, H.; Kreutzer, M.; Jones, P. G. *Angew. Chem.* **1991**, *103*, 1148. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1127. For a reaction of the peripheral C═C bond see: Khodorkovsky, V. Y.; Becker, J. Y.; Bernstein, J. *Synthesis* **1992**, 1071.

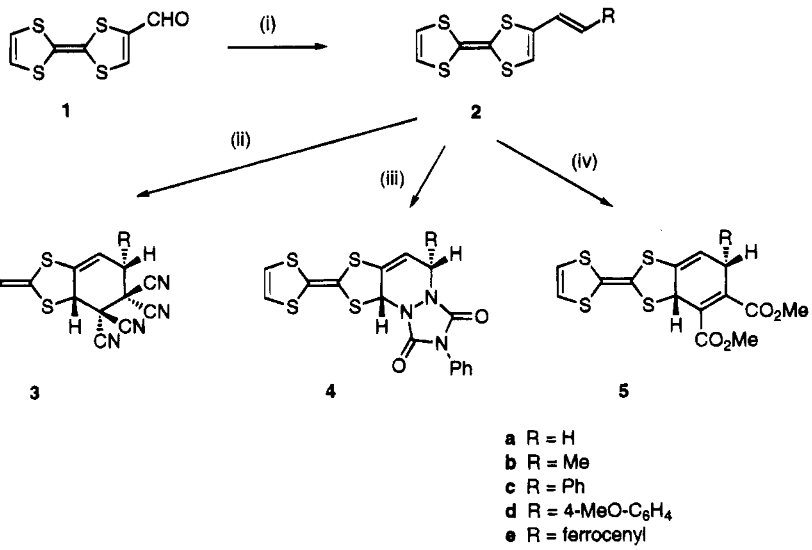
[6] The prototype model system for molecular rectification is a covalent TTF-σ-TCNQ (TCNQ = tetracyano-*p*-quinodimethane) derivative in which the donor and acceptor units are linked by a rigid spacer unit (Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277). This proposed molecule has not yet been synthesised; however, analogues with flexible spacers have been obtained (Metzger, R. M.; Panetta, C. A. *J. Mol. Elect.* **1989**, *5*, 1. *Idem. Mat. Res. Soc. Symp. Proc.* **1990**, *173*, 531. Metzger, R. M. In *Molecular and Biomolecular Electronics;* Birge, R. R., Ed.; American Chemical Society: Washington, D.C., 1994; Chapter 5). Compound **2e** reacts with TCNQ (acetonitrile, reflux) to afford an unidentified pale yellow solid which is a 1:1 adduct (based on C,H,N combustion analysis); the corresponding mass was not seen in the mass spectrum, and the ^{1}H NMR spectrum consists of broad peaks characteristic of a radical species.

[7] Bryce, M. R.; Davison, G. R.; Gough, S. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2571.

[8] Green and Allen (ref 3a) report that compound **2a** is unstable: in our hands this is not the case, and pure compound **2a** was stored at room temperature for several months without observable decomposition.

0022-3263/95/1960-4644$09.00/0 © 1995 American Chemical Society

Scheme 1[a]



[a] (i) $Ph_3PCHR^+ X^-$, *n*-BuLi, THF, −78 °C; (ii) TCNE, toluene, reflux; (iii) NPTD, toluene, reflux; (iv) DMAD, toluene, reflux.

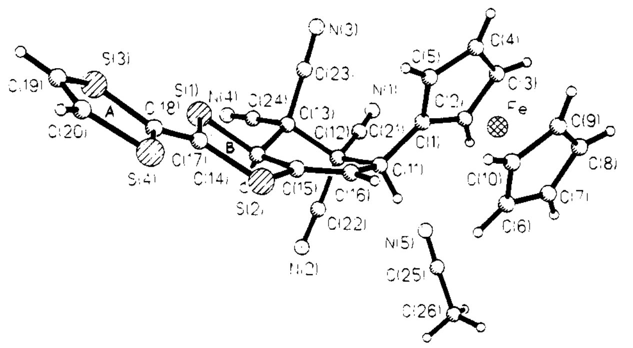


Figure 1. Asymmetric unit of **3e**·MeCN crystal.

1-[2,2′-Bi(1,3-dithiolylidene)-4-yl]propylene (2b). Ethyltriphenylphosphonium bromide (1.0 g, 2.70 mmol), butyllithium (1.7 mL, 1.6 M, 2.72 mmol), and **1** (500 mg, 2.16 mmol) afforded **2b** as a dark orange oil (1:4 *cis*:*trans* isomer ratio) (420 mg, 80% yield); *m*/*z* (DCI) 245 ($M^+ + 1$), HRMS found 243.9428, $C_9H_8S_4$ requires 243.9509; δ_H ($CDCl_3$) 6.58 (2H, s), 6.45 (1H, s), 6.35 (1H, d, J =15.4 Hz), 5.60 (1H, m), 1.81 (3H, m).

***trans*-1-[2,2′-Bi(1,3-dithiolylidene)-4-yl]-2-phenylethylene (2c).** Benzyltriphenylphosphonium chloride (2.0 g, 5.14 mmol), butyllithium (3.3 mL 5.28 mmol), and **1** (1.0 g, 4.31 mmol) afforded **2c** as a purple solid (1.02 g, 77% yield); mp 124−126 °C. (Found: C, 54.8; H, 3.2. $C_{14}H_{10}S_4$ requires C, 54.9; H, 3.3%); *m*/*z* (DCI) 307 ($M^+ + 1$); δ_H (d_6-acetone) 7.76−7.31 (5H, m), 7.20 (1H, d, J = 15.9 Hz), 6.81 (1H, s), 6.66 (2H, s), 6.47 (1H, d, J =15.6 Hz).

***trans*-1-[2,2′-Bi(1,3-dithiolylidene)-4-yl]-2-(4-methoxyphenyl)ethylene (2d).** (4-Methoxybenzyl)triphenylphosphonium chloride (1.0 g, 2.39 mmol), butyllithium (1.5 mL, 2.40 mmol) and **1** (500 mg, 2.16 mmol) afforded **2d** as a dark orange solid (600mg, 83% yield); m.p. 164−167 °C. (Found: C, 53.5; H, 3.4. $C_{15}H_{12}OS_4$ requires C, 53.5; H, 3.6%); *m*/*z* (DCI) 337 ($M^+ + 1$); δ_H (d_6-DMSO) 7.46 (2H, d, J = 8.7 Hz), 7.05 (1H, d, J = 16.1 Hz), 6.90 (2H, d, J = 8.8 Hz), 6.81 (1H, s), 6.73 (2H, s), 6.33 (1H, d, J = 16.0 Hz), 3.74 (3H, s).

***trans*-1-{2-[2,2′-Bi(1,3-dithiolylidene)-4-yl]vinyl}ferrocene (2e).**[4b] (Methylferrocenyltriphenylphosphonium iodide[9] (3.5 g, 5.96 mmol), butyllithium (3.7 mL, 6.00 mmol) and **1** (1.0 g, 4.31 mmol) afforded a mixture of *cis* and *trans* isomers of **2e** (1.28 g, 72% yield). The *trans* isomer was isolated pure by fractional recrystallization from toluene as a purple solid (1.03 g, 58% yield): mp 186−187 °C. (Found: C, 52.4; H, 3.5. $C_{18}H_{14}FeS_4$ requires C, 52.2; H, 3.4%); *m*/*z* (DCI) 415 ($M^+ + 1$); δ_H (d_6-acetone) 6.73 (1H, d, J = 15.8 Hz), 6.65 (2H, s), 6.58 (1H, s), 6.25 (1H, d, J = 15.5 Hz), 4.52 (2H, m), 4.32 (2H, m), 4.14 (5H, s).

General Procedure for Compounds 3a−e. A solution of vinyl-TTF derivative **2a−e** and tetracyanoethylene in toluene (10 mL) was refluxed for 16 h. After evaporating the mixture under reduced pressure, column chromatography using silica gel and toluene as the eluent afforded the product **3a−e** which was recrystallized from dichloromethane.

2-(1,3-Dithiol-2-ylidene)-3a,4,5,6-tetrahydro-1,3-benzodithiole-4,4,5,5-tetracarbonitrile (3a). Vinyltetrathiafulvalene **2a** (200 mg, 0.87 mmol) and tetracyanoethylene (250 mg, 1.95 mmol) afforded **3a** as a yellow solid (220 mg, 70% yield): mp 190−192 °C. (Found: C, 46.9; H, 1.7. N, 14.8; $C_{14}H_6N_4S_4$ requires C, 46.9; H, 1.7; N, 15.6%); *m*/*z* (DCI) 359 ($M^+ + 1$), HRMS found 357.9253, $C_{14}H_6N_4S_4$ requires 357.9475; δ_H ($CDCl_3$) 6.43 (1H, AB, J_{AB} = 6.4 Hz), 6.35 (1H, AB, J_{AB} = 6.4 Hz) 5.86 (1H, m), 4.89 (1H, m), 3.86 (2H, m); υ_{max}(KBr)/cm^{-1} 2254 (CN).

2-(1,3-Dithiol-2-ylidene)-6-methyl-3a,4,5,6-tetrahydro-1,3-benzodithiole-4,4,5,5-tetracarbonitrile (3b). Compound **2b** (200 mg, 0.82 mmol) and tetracyanoethylene (110 mg, 0.86 mmol) afforded **3b** as an orange/brown solid (170 mg, 56% yield): mp 192−194 °C; *m*/*z* (DCI) 373 (M^++ 1), HRMS found 371.9605, $C_{15}H_8N_4S_4$ requires 371.9632; δ_H ($CDCl_3$) 6.44 (1H, AB, J_{AB} = 6.5 Hz), 6.36 (1H, AB, J_{AB} = 6.5 Hz), 5.90 (1H, m), 4.90 (1H, m), 3.43 (1H, m), 1.75 (3H, d, J = 7.6 Hz); υ_{max} (KBr)/cm^{-1} 2251 (CN).

2-(1,3-Dithiol-2-ylidene)-6-phenyl-3a,4,5,6-tetrahydro-1,3-benzodithiole-4,4,5,5-tetracarbonitrile (3c). Compound **2c** (200 mg, 0.65 mmol) and tetracyanoethylene (90 mg, 0.70 mmol) afforded **3c** as an orange/brown solid (170 mg, 59% yield): mp 106−108 °C; *m*/*z* (DCI) 435 ($M^+ + 1$), HRMS found 433.9779, $C_{20}H_{10}N_4S_4$ requires 433.9788; δ_H ($CDCl_3$) 7.49 (5H, broad s), 6.46 (1H, AB, J_{AB} = 6.5 Hz), 6.38 (1H, AB, J_{AB} = 6.5 Hz), 6.14 (1H, m), 4.94 (1H, m), 4.51 (1H, m); υ_{max} (KBr)/cm^{-1} 2253 (CN).

2-(1,3-Dithiol-2-ylidene)-6-(4-methoxyphenyl)-3a,4,5,6-tetrahydro-1,3-benzodithiole-4,4,5,5-tetracarbonitrile (3d). Compound **2d** (100 mg, 0.30 mmol) and tetracyanoethylene (40 mg, 0.31 mmol) afforded **3d** as an orange solid (100 mg, 75% yield): mp 164−166 °C; *m*/*z* (EI) 464, HRMS found 463.9899, $C_{21}H_{12}N_4OS_4$ requires 463.9894; δ_H ($CDCl_3$) 7.40 (2H, d, J = 8.7 Hz), 6.97 (2H, d, J = 8.8 Hz), 6.46 (1H, AB, J_{AB} = 6.5 Hz), 6.38 (1H, AB, J_{AB} = 6.5 Hz), 6.11 (1H, m), 4.93 (1H, m), 4.49 (1H, m), 3.85 (3H, s); υ_{max} (KBr)/cm^{-1} 2250 (CN).

2-(1,3-Dithiol-2-ylidene)-6-[bis(ηcyclopentadienyl)iron]-3a,4,5,6-tetrahydro-1,3-benzodithiole-4,4,5,5-tetracarbonitrile (3e). A solution of **2e** (50 mg, 0.12 mmol) in hot acetonitrile (3 mL) was added to a solution of tetracyanoethylene (15 mg, 0.12 mmol) in acetonitrile (5 mL), and the mixture was refluxed for 5 min. The solution was cooled to 20 °C and after 16 h the

---

(9) Pauson, P. L.; Watts, W. E. *J. Chem. Soc.* **1963**, 2990.

product was filtered and washed with ice-cold acetonitrile. Yellow crystals of **3e**·MeCN were harvested for X-ray analysis, together with **3e** as a yellow powder (45 mg, 68% combined yield). Data for **3e**: mp >250 °C. (Found: C, 53.1; H, 2.6; N, 11.1. $C_{24}H_{14}FeN_4S_4$ requires C, 53.1; H, 2.6; N, 10.3%); *m/z* (DCI) 543 ($M^+ + 1$); δ_H (CD_2Cl_2) 6.54 (1H, m), 6.50 (1H, AB, J_{AB} = 6.5 Hz), 6.43 (1H, AB, J_{AB} = 6.5 Hz), 5.00 (1H, m), 4.68 (1H, m), 4.46 (2H, t, J = 1.3 Hz), 4.35 (2H, t, J =1.4 Hz), 4.27 (5H, s); υ_{max} (KBr)/cm^{-1} 2198 (CN).

2-(1,3-Dithiol-2-ylidene)-6-(4-methoxyphenyl)-*N*-phenyl-3a,4,5,6-tetrahydro-1,3-dithiolo[2,3-*c*]pyridazine-4,5-dicarboximide (4d). To a solution of **2d** (250 mg, 0.74 mmol) in toluene (10mL) was added 4-phenyl-1,2,4-triazoline-3,5-dione (150 mg, 0.86 mmol). The mixture was refluxed for 4 h. Column chromatography using silica gel and toluene as the eluent removed excess starting material. Subsequent use of dichloromethane–acetone (2:1 v/v) as the eluent gave **4d** as an orange solid, which was recrystallized from toluene (230 mg, 61% yield); mp 134–137 °C. (Found: C, 53.9; H, 3.5; N, 7.9. $C_{23}H_{17}N_3O_3S_4$ requires C, 54.0; H, 3.4; N, 8.2%); *m/z* (DCI) 512 ($M^+ + 1$); δ_H ($CDCl_3$) 7.40 (7H, m), 6.90 (2H, d, J = 8.7 Hz), 6.37 (1H, AB, J_{AB} = 6.6 Hz), 6.28 (1H, AB, J_{AB} = 6.6 Hz), 5.96 (1H, m), 5.62 (2H, m) and 3.79 (3H, s); υ_{max} (Nujol)/cm^{-1} 1775 and 1708 (both C=O).

2-(1,3-Dithiol-2-ylidene)-6-[bis(η-cyclopentadienyl)iron]-*N*-phenyl-3a,4,5,6-tetrahydro-1,3-dithiolo[2,3-*c*]pyridazine-4,5-dicarboximide (4e). Following the procedure described above for **4d**, **2e** (100 mg, 0.24 mmol) and 4-phenyl-1,2,4-triazoline-3,5-dione (45 mg, 0.26 mmol) gave **4e** as an orange solid, which was recrystallized from toluene (45 mg, 33% yield): mp 199–201 °C; *m/z* (DCI) 590 ($M^+ + 1$), HRMS found 588.9494, $C_{26}H_{19}FeN_3O_2S_4$ requires 588.9710; δ_H ($CDCl_3$) 7.40 (5H, m), 6.38 (1H, AB, J_{AB} = 6.6 Hz), 6.29 (1H, AB, J_{AB} = 6.6 Hz), 6.36 (1H, s), 5.50 (2H, m), 4.53 (1H, s), 4.21 (8H, s); υ_{max} (KBr)/cm^{-1} 1772 and 1719 (both C=O).

Dimethyl 2-(1,3-dithiol-2-ylidene)-3a,6-dihydro-1,3-benzodithiole-4,5-dicarboxylate (5a). To a solution of **2a** (200 mg, 0.87 mmol) in toluene (15 mL) was added dimethyl acetylenedicarboxylate (0.1 mL, 0.81 mmol), and the mixture was refluxed for 16 h. The solvent was evaporated under reduced pressure and the residue chromatographed using neutral alumina and toluene as the eluent to give **5a** as a red solid, after sequential recrystallization from methanol and then from dichloromethane–hexane (150 mg, 46% yield); mp 146–149 °C. (Found: C, 44.7; H, 3.1. $C_{14}H_{12}O_4S_4$ requires C, 45.2; H, 3.3%); *m/z* (DCI) 373 ($M^+ + 1$); δ_H ($CDCl_3$) 6.35 (1H, AB, J_{AB} = 6.5 Hz), 6.26 (1H, AB, J_{AB} = 6.5 Hz), 6.12 (1H, d, J = 2.4 Hz), 4.70 (1H, m), 3.83 (3H, s), 3.78 (3H, s), 3.20 (1H, m), 2.74 (1H, m); υ_{max} (KBr)/cm^{-1} 1706 (C=O).

Crystal structure analysis of 3e: $C_{24}H_{14}FeN_4S_4{\cdot}CH_3CN$, M = 583.5 space group $P\bar{1}$, T = 293 K, a = 7.008(2), b = 11.660(3), c = 17.065(4) Å, α = 80.43(2), β = 82.46(2), γ = 74.27(2)°, Z = 2, U = 1318.2(5) Å^3 (from 25 reflections with $10 < \theta < 12°$), $F(000)$ = 596, graphite monochromated Mo K_α radiation, λ = 0.71073 Å, μ = 9.1 cm^{-1}. Data collection: Rigaku AFC6S four-circle diffractometer, $2\theta/\omega$ scan mode, partial decomposition of the crystal occurred during the experiment (three standards declined by an average of 22%), 4309 independent reflections measured, semiempirical absorption correction[10] (108 ψ-scans of three reflections, $T_{min}:T_{max}$ = 0.8015) using TEXSAN programs.[11] The structure was solved by direct methods.[12] All non-hydrogen atoms were refined with anisotropic displacement parameters (with riding H atoms) by full-matrix least squares[13] (325 variables, against F's of 2870 reflections with $F > 4\sigma(F)$, weighting scheme $w = [\sigma^2(F) + 0.0002\,F^2]^{-1}$) to R = 0.038, wR = 0.047, S = 1.72, $\Delta\varrho_{max}$ = 0.25 eÅ^{-3}. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Acknowledgment. We thank Dr. S. T. A. K. Daley for helpful discussions, EPSRC and Zeneca FCMO for funding this work, and The Nuffield Foundation for a Science Research Fellowship (to M.R.B.).

JO9500491

---

[10] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

[11] TEXSAN, Version 5.1, 1989, Molecular Structure Corp., The Woodlands, TX 77381.

[12] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

[13] Sheldrick, G. M. SHELXTL PLUS, Göttingen and Siemens plc, 1990.