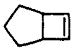
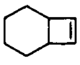
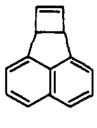
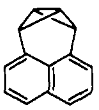
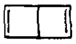
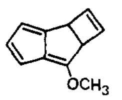
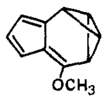
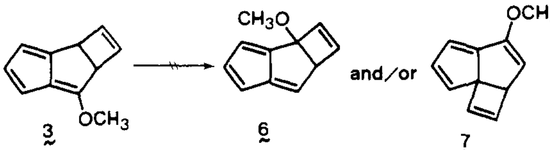
Table I. Activation Energies for Cyclobutene and Bicyclobutane Ring Openings

compd	E_a, kcal/mol	ref	compd	E_a, kcal/mol	ref
	45.9	a		38.8	g
	43.2	b		32.4	g
	39.5	c			
	39.3	d		32.9	d
	23.0	e		25.9	h
	36.7	f		~31	f

[a] Branton, G. R.; Frey, H. M.; Montagne, D. C.; Stevens, D. D. R. *Trans. Faraday Soc.* 1966, *62*, 659. [b] Branton, G. R.; Frey, H. M.; Skinner, R. F. *Ibid.* 1966, *62*, 1546. [c] Willcott, M. R.; Coerland, E. *Tetrahedron Lett.* 1966, 6341. [d] Reference 4g. [e] Reference 1b. [f] This work. [g] Christl, M.; Heinemann, V.; Kristof, W. *J. Am. Chem. Soc.* 1975, *97*, 2299. [h] Reference 11.

behavior of **2** and **3** is of particular interest. It should be noted that **3** was found to be thermally stable up to 120 °C in dodecane or benzene for 48 h; consequently the intervention of **3** during the thermal isomerization of **2** to **1** can be eliminated. However, at elevated temperature **3** undergoes clean isomerization to **1** quantitatively with first-order kinetics in the temperature range 428–455 K (by ^{1}H NMR monitoring in benzene-d_6).[10] From an Arrhenius plot (r = 0.9986) of the data the activation parameters, $\Delta H^\ddagger = 35.8 \pm 0.6$ kcal/mol, $\Delta S^\ddagger = 2.1 \pm 1.0$ eu, $E_a = 36.7 \pm 0.6$ kcal/mol, and log $A = 13.9 \pm 0.2$ are obtained. The azulvalene **2** also converted (70–80%) thermally to **1** accompanied by partial decomposition. From the several runs the activation energy for the process was roughly estimated to be 31 kcal/mol, deduced from the decay rate of **2** in dodecane (temperature range 110–140 °C) monitored by UV spectroscopy. In Table I available data of activation energies for the related compounds are compared. Inspection of these data indicate that the activation energies for the ring opening of both **2** and **3** are substantially higher than those of benzvalene and Dewar benzene, respectively; however, the values found for **2** and **3** are smaller than those of the other compounds in Table I.

In conclusion, two points we believe are worth making. First, although most bicyclobutanes incorporated into a cyclic framework are known to be thermally converted to the corresponding cyclobutene isomer, the thermolysis of **2** gives rise directly to **1** without any intervention of **3**. The plausible explanation for the process is that the fulvene π system (6π) in **2** does not play a passive role during this ring opening but assists in the fission of the bicyclobutane ring.[11] Second, in spite of the fact that the activation enthalpy for aromatization of **3** is greater than that of Dewar benzene, **3** did not give any detectable amount of either **6** or **7** through a [3,7] sigmatropic shift during the thermolysis



3 6 7

of **3**.[12,13] These facts found for **2** and **3** are, at least phenomenalistically, parallel to the thermal behavior of benzvalene and Dewar benzene, respectively. The possibility of realizing the synthesis of both parent azulvalene and Dewar azulene and the study on the ground- and excited-states properties of these intriguing molecules are currently under investigation.

Registry No. 1, 58000-25-2; **2**, 79794-93-7; **3**, 82182-27-2; **4**, 79815-07-9.

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(9) We examined here direct irradiation in hexane and acetone-sensitized irradiation and low-temperature irradiation in methylcyclohexane–isopentane (1:4) at 77 K; all resulted in decomposition. In all cases, irradiations were conducted with a high-pressure Hg lamp through Pyrex and/or quartz filter.

(10) A solution of **3** in benzene-d_6 was degassed and sealed in vacuo in an NMR tube. The tube was immersed in a thermostated and stirred oil bath. The tube was removed at appropriate intervals and immediately cooled to room temperature. The disappearance of **3** and the appearance of **1** were monitored by NMR integration. First-order rate constants are $k^{428} = 1.24 \times 10^{-5}$, $k^{438} = 3.66 \times 10^{-5}$, $k^{447} = 8.00 \times 10^{-5}$, and $k^{455} = 1.66 \times 10^{-4}$ s^{-1}.

(11) In the case of thermal conversion of benzvalene to benzene it was suggested that the extra double bond does not play a passive role in this process: Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1975**, *97*, 2932. Turro, N. J.; Renner, C. A.; Katz, T. J.; Wiberg, K. B.; Connon, H. A. *Tetrahedron Lett.* **1976**, 4133.

(12) Previous studies by Goldstein and Leight have shown that ^{1}H NMR spectra of deuterated Dewar benzene recovered after half thermal cyclodissociation revealed less than 5% contamination by any isotopic isomer: Goldstein, M. J.; Leight, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 8112.

(13) For a general discussion of a formal [3,3] sigmatropic shift, see: Otterbacher, E. W.; Gajewsky, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 5862 and references cited therein. In view of the facts that the fulvene acts as a 6π component in pericyclic reactions and that Dewar benzene isomerizes to benzene even at room temperature whereas Dewar azulene **3** isomerizes only at elevated temperature, a [3,7] sigmatropic shift in **3** would have, a priori, been expected.

Long-Distance (25 Å) Electron Transfer by Triplet Excited States in Rigid Media[1]

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Received April 22, 1982

We report measurements of phosphorescence quenching in rigid media by two types of electron-transfer reactions (see Table I for data and key to abbreviations):

$$\mathrm{TMPD(T_1)} + \mathrm{PA} \rightarrow \mathrm{TMPD^+} + \mathrm{PA^-} \qquad (1)$$

$$\mathrm{HMTI} + \mathrm{PMDA(T_1)} \rightarrow \mathrm{HMTI^+} + \mathrm{PMDA^-} \qquad (2)$$

In reaction 1 the first triplet excited state (T_1) of TMPD transfers an electron *to* phthalic anhydride (PA); in reaction 2 triplet PMDA captures an electron *from* an unexcited molecule of HMTI. These reactions show similar 25-Å quenching distances obtained by using eq 3 below. Although back reactions are expected to prevent a measurable buildup of the ions in reactions 1 and 2 and no ions were found, the data are in excellent accord with the electron-transfer mechanism while alternatives may be eliminated (see below). Charge-transfer processes of triplets occur in fluid solutions[3-6] where the reactants may collide with each other, but long-distance electron transfer (ET) by triplets has not been previously reported. The 25-Å quenching radii found here are the largest reported for ET by excited molecules.

Quenching data for reaction 1 appear in Figure 1. The phosphorescence and fluorescence intensities were measured in

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(1) Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE under Contract No. W-31-109-ENG-38.

(2) Undergraduate research participants from (a) University of Michigan at Flint and (b) University of Chicago.

(3) Ibar, S.; Linschitz, H.; Cohen, S. *J. Am. Chem. Soc.* **1980**, *102*, 1419.

(4) Periasamy, N.; Linschitz, H. *Chem. Phys. Lett.* **1979**, *64*, 281.

(5) Cheddar, G.; Castelli, F.; Tollin, G. *Photochem. Photobiol.* **1980**, *32*, 71.

(6) Cheddar, G.; Tollin, G. *Photobiochem. Photobiophys.* **1980**, *1*, 235.

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Table I. Quenching Radii, Excited-State Lifetimes, and Electron-Transfer Energetics for Phosphorescence and Fluorescence Quenching in Solids

					energetics, eV	
reaction, D + A[a]	S[a]	R, Å	τ[b]	E*,[c] eV	ΔG-(D^+A^-)[d]	$-\Delta G°_{ET}$[e]
TMPD(S_1) + PA	M	17 ± 1	7 ns	3.5	1.4	2.1
TMPD(T_1) + PA	M	25 ± 1	3 s	2.9	1.4	1.5
Et_6Bz + PMDA(T_1)	T	29 ± 4	7 s	3.1	~2.1	1.0
HMTI + PMDA(T_1)	T	26 ± 4	7 s	3.1	~2.1	1.0
IPCz(S_1) + TCNE	T	<19[f]	18 ns	3.6	0.9	2.7
IPCz(T_1) + TCNE	T	33 ± 7	7 s	3.1	0.9	2.2

[a] Solvent: M = 2-methyltetrahydrofuran (MTHF) at 77 K, T = triacetin–tributyrin (70:30 v/v) at 196 K. Solutes: TMPD = *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, PA = phthalic anhydride, Et_6Bz = hexaethylbenzene, HMTI = hexamethyltriindan (a very highly hindered hexaalkylbenzene), IPCz = *N*-isopropylcarbazole, TCNE = tetracyanoethylene, PMDA = pyromellitic dianhydride. [b] Excited-state lifetime. [c] Excited-state energy. Quencher excited-state energies (singlet, triplet) are PA (>3.5, 3.0), Et_6Bz and HMTI (4.4, 3.4), and TCNE (4.3, ?). [d] Free-energy change for the reaction $D + A \rightarrow D^+ + A^-$ from electrochemical data in polar fluids. The appropriate value in our rigid matrices will be larger by a few tenths of an eV. [e] Free-energy change for the quenching reaction $D^* + A$ or $D + A^* \rightarrow D^+ + A^-$, $\Delta G°_{ET} = \Delta G(D^+ A^-) - E^*$. The values will be too negative as noted in *d*. [f] Only upper limit determined due to scatter of data.

2-methyltetrahydrofuran (MTHF) glass at 77 K in degassed, sealed cells by a Perkin-Elmer MPF-44B spectrofluorimeter. Both fluorescence (λ_{max} 386 nm) and phosphorescence (λ_{max} 466 nm) decreased exponentially with increasing quencher concentration, *c* as follows:

$$I/I_0 = \exp(-vc) = \exp(-{}^4\!/_3\pi R^3 c) \qquad (3)$$

with phosphorescence quenching more than 3 times as effective as fluorescence quenching on a per concentration basis. At our highest concentration of phthalic anhydride, 0.1 M, 98% of the phosphorescence is quenched. In eq 3 the concentration, *c*, of quenchers is in number/unit volume units.[7] *R* is the (center to center) distance at which the quenching rate equals the normal phosphorescence (or fluorescence) decay rate.[8]

Long-distance electron transfer (ET) by radical ions[9,10] or trapped electrons[11] was shown to occur over distances of 10–40 Å wih rate constants *k* decreasing exponentially with distance:

$$k(r) = \nu \exp[-(r - R_0)/a] \qquad (4)$$

where the frequency factors ν had a maximum value of 10^{13}–10^{16} s^{-1} and the range parameters, *a*, were usually 0.5–1.0 Å.[9-11] R_0, which corrects for the finite size of the reactants, is about 6 Å.

Since ET rates by excited states are also expected to decrease rapidly with distance as in eq 4, we can give eq 3 the following simple interpretation: any excited molecule that has at least one quencher at a distance closer than the quenching radius *R* will be quenched by ET; all others will phosphoresce (or fluoresce) normally. Eq 3 can be derived on this simple basis, and more exact calculations[8] show it to be very accurate even though the dividing line between quenched and unquenched molecules is not actually a step function at *R* but changes gradually over a narrow region of $\approx\pm 2a$ around *R*. The quenching radius *R* where $k(r) = \tau^{-1}$ is

$$R \cong R_0 + a \ln \nu\tau \qquad (5)$$

where τ is the appropriate phosphorescence or fluorescence lifetime.

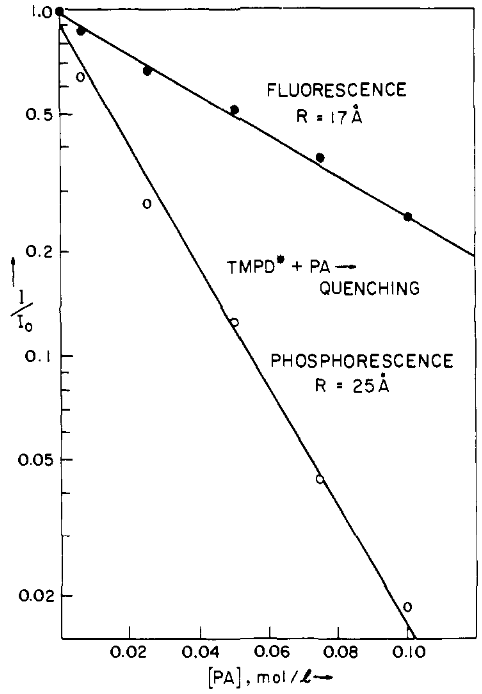

Figure 1. Decrease of fluorescence and phosphorescence intensities of excited TMPD as a function of the concentration of the electron-acceptor phthalic anhydride in MTHF glass at 77 K. The long-distance electron transfer radii, *R*, were obtained from these data by using eq 3.

The observed phosphorescence quenching radii of ≈25 Å for reactions 1 and 2 are a little shorter than the 29–35-Å maximum ET distances measured at $t = \tau_p \cong 3$ s for radical ions. Those distances are measured by pulse radiolysis experiments on charge transfer from several radical ions to the best acceptors—those having optimal reaction exothermicity to maximize ν of eq 4. The radii found here for ET by triplets may be slightly shorter because the exothermicities of reactions 1 and 2 are perhaps not of optimal exothermicity (smaller ν). It is also possible that these triplet ET reactions have rates that decrease more rapidly with distance (smaller *a*) than the rates of radical ion reactions do.

It is worth noting that we can conceive of two alternatives to the ET mechanism, but neither of these alternative mechanisms can explain the experimental facts. The first, quenching by electronic energy transfer in either the Förster or exchange mechanism, was excluded by choosing quenchers having excited-state energies higher than those of our excited molecules TMPD or PMDA (see Table I). The second alternative, formation of nonemmissive charge-transfer complexes with the quenchers, cannot explain why phosphorescence is quenched far more effectively than fluorescence. This difference is expected in the ET mechanism due to the much longer lifetimes of phosphorescence (see eq 5). Complexing should also give rise to Stern–Volmer quenching kinetics, $I_0/I = 1 + Kc$, that completely fail to fit the data. Also, new absorptions or emissions were not observed, with the exception of a small absorption at 375 nm in the TMPD–PA system. This band appears only when both solutes are present, and its intensity increases (reversibly) at low temperature, indicating that it is due to the CT complex. But its intensity increases linearly with PA concentration to 0.75 M. Thus we may conclude that at the highest PA concentration (0.1 M) used in the quenching experiments, where 98% phosphorescence quenching occurred, less than 10% of the TMPD was complexed,[12] and the effects of complexing are negligible. A more elegant demonstration of the

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(7) If the quenching volume $v = 4\pi R^3/3$ is expressed in $Å^3$, *c* is 6.02 × 10^{-4} times the molar concentration.

(8) Inokuti, M.; Hirayama, F. *J. Chem. Phys.* **1965**, *43*, 1978.

(9) Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6746.

(10) Miller, J. R. *Science (Washington, D.C.)* **1975**, *181*, 221.

(11) Beitz, J. V.; Miller, J. R. *J. Chem. Phys.* **1979**, *71*, 4579.

(12) The absorbance at 375 nm is 0.35 in a sample containing 0.01 M TMPD and 0.75 M PA at 77 K. If 10% of the TMPD were complexed, then the molar extinction coefficient of the complex is $\epsilon_{375} = 1.1 \times 10^3$. Known CT complexes of TMPD have similar or larger ϵ,[13] supporting this ≤10% estimate.

(13) Foster, R. "Organic Charge Transfer Complexes", Academic Press: New York, 1969.

ET mechanism will be measurement of the dynamic, time-dependent quenching predicting to occur in the solid state by eq 4. These experiments are in progress.

Acknowledgment. We thank Gerhard Closs for encouragement and advice and Kurt Huddleston for helpful discussions.

Registry No. TMPD, 100-22-1; PA, 85-44-9; Et_6Bz, 604-88-6; PMDA, 89-32-7; HMTI, 40650-56-4; IPCz, 1484-09-9; TCNE, 670-54-2.

Hydrogenation and Reduction of Nitrogen-Containing Heteroaromatics. Electron-Transfer and Radical-Induced Dimerization of Phthalazine

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Received May 19, 1981

In our continuing investigation of exchange and electron transfer in bis(η^5-cyclopentadienyl)titanium systems, we have studied $Cp_2Ti(bpy)$ (bpy = 2,2-bipyridyl) and have found it to possess a triplet excited state that is thermally accessible from the ground state singlet.[3] Other examples of this intramolecular electron transfer have been observed in various Cp_2Ti complexes of substituted 1,10-phenanthrolines. Recently,[4] we reported an example of intramolecular electron-transfer-inducing methyl group carbon–hydrogen bond dissociation in bis(η^5-cyclopentadienyl)titanium complexes of 4-methyl-substituted 1,10-phenanthrolines. In this communication, we report that the reaction of $Cp_2Ti(CO)_2$ with phthalazine results in electron transfer upon complexation, leading to the formation of a bimolecular complex—bis[bis(η^5-cyclopentadienyl)(phthalazine)titanium] (II).

The complex is prepared[5] by reaction of $Cp_2Ti(CO)_2$ with the ligand in THF under an inert atmosphere. The air-sensitive product was examined by electron-impact mass spectrometry. The mass spectrum showed a weak parent molecular ion at 616, indicating a dimeric product, as well as a major ion peak at 309, one mass unit greater than that expected for the parent peak of monomeric bis(η^5-cyclopentadienyl)(phthalazine)titanium.

The molecular geometry resulting from a single-crystal X-ray structural determination[6] is shown in Figure 1. Important bond distances and angles are given in Table I. The molecule in Figure 1 has two monomeric units related by a C_2 axis. The Ti–Ti distance is 6.17 Å, and the dihedral angle between the two ligands is 78.1°. The two units are bridged by a C(8)–C(8)′ carbon–carbon bond of 1.625 (10) Å, which is considerably longer than usually found for carbon–carbon paraffinic bonds (1.54 Å). A dihedral angle of 11.6° between the ligand and the Ti–N(1)–N(2) plane is observed. This "bent" geometry may be the result of electronic factors as was similarly observed and discussed for $Cp_2Ti(bpy)$.[3]

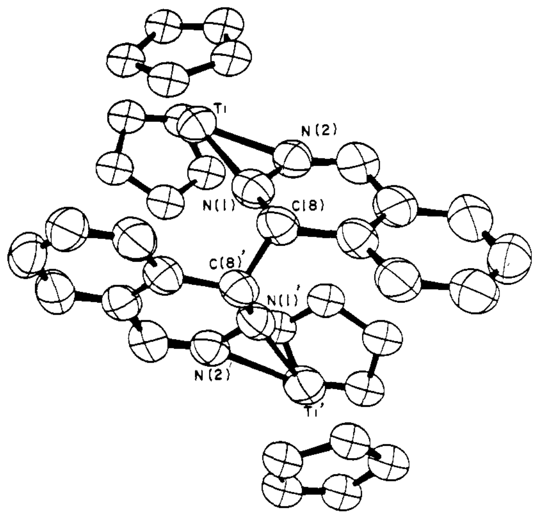

Figure 1. Molecular structure of bis[bis(η^5-cyclopentadienyl)(phthalazine)titanium].

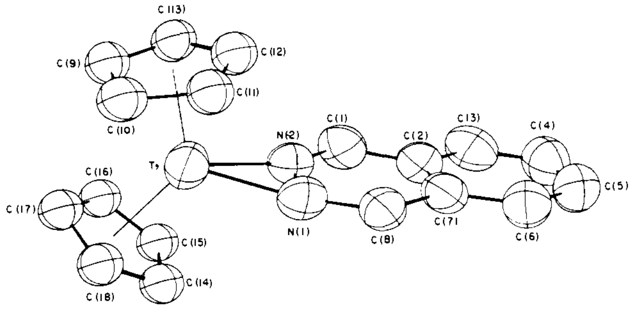

Figure 2. Molecular structure of the monomeric unit of bis[bis(η^5-cyclopentadienyl)(phthalazine)titanium].

Table I. Important Interatomic Bond Distances (Å) and Angles (deg) in Bis[bis(η^5-cyclopentadienyl)(phthalazine)titanium]

Ti–N(1)	2.075 (5)	N(1)–Ti–N(2)	37.2 (2)
Ti–N(2)	2.116 (5)	Ti–N(1)–N(2)	73.0 (3)
N(1)–N(2)	1.338 (6)	Ti–N(2)–N(1)	69.8 (3)
N(1)–C(8)	1.436 (7)	N(2)–N(1)–C(8)	121.9 (4)
C(1)–N(2)	1.284 (7)	C(1)–N(2)–N(1)	124.8 (5)
C(1)–C(2)	1.441 (8)	N(2)–C(1)–C(2)	120.2 (6)
C(2)–C(7)	1.396 (8)	C(1)–C(2)–C(7)	118.9 (5)
C(7)–C(8)	1.525 (7)	C(2)–C(7)–C(8)	119.5 (5)
C(8)–C(8)′	1.625 (10)	C(7)–C(8)–N(1)	112.5 (5)

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(1) To whom correspondence should be addressed.

(2) (a) E. I. du Pont de Nemours & Company, Central Research and Development, Experimental Station. (b) University of Illinois. (c) Argonne National Laboratory.

(3) McPherson, A. M.; Fieselmann, B. F.; Lichtenberger, D. L.; McPherson, D. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 3425.

(4) Corbin, D. R.; Willis, W. S.; Duesler, E. N.; Stucky, G. D. *J. Am. Chem. Soc.* **1980**, *102*, 5969.

(5) Compound preparation: dicarbonylbis(η^5-cyclopentadienyl)titanium(II) (0.45 g, 2.0 mmol) is added to a solution of phthalazine (0.26 g, 2.0 mmol) in approximately 80 mL of THF under an inert atmosphere. For 12 h, the mixture is stirred with moderate heating. The solvent is then removed under reduced pressure. The product is washed with refluxing hexanes and extracted with refluxing toluene. The filtrate is heated to reflux and allowed to cool slowly. After a short time, crystals form. Anal. Calcd for $C_{36}H_{32}N_4Ti_2$: C, 70.14; H, 5.23; N, 9.09; Ti, 15.54. Found: C, 70.68; H, 5.22; N, 8.89; Ti, 15.60.

(6) Crystal Data: $C_{36}H_{32}N_4Ti_2$, mol wt 616.48; monoclinic; $a = 17.57$ (1), $b = 8.232$ (3), $c = 21.35$ (1) Å; $\beta = 106.41$ (4)°; $Z = 4$; $d_{calcd} = 1.38$ g cm^{-3}; space group C_2/n. Cell and intensity data were collected on a syntex $P2_1$ diffractometer using Mo Kα radiation ($\lambda = 0.71069$ Å). Measurements were made to $2\theta = 50°$ for a total of 5761 independent reflections of which 1062 were rejected as being systematically absent. With the criterion $F_o^2 > 3\sigma(F_o)^2$, 1514 reflections were considered observed. A total of 2454 unique reflections were in the refinement of the structure. The structure was solved with direct methods in the SHELX program package[7] with $\omega(|F_o| - |F_c|)^2$ being the function minimized during the least-squares refinement. Intensity statistics strongly suggested the centrosymmetric space group $C2/c$. Fourier and difference Fourier analyses provided all the non-hydrogen-atom positions. Least-squares refinement with anisotropic temperature factors for the non-hydrogen atoms with hydrogen atoms included at calculated positions of 0.95 Å and statistical weights led to R_2 $(=(\sum\omega||F_o| - |F_c||^2/\sum\omega|F_o|^2)^{1/2}) = 0.066$. Due to a large number of correlation coefficients greater than 0.5 between the x and z parameters, a reindexing of the cell was undertaken. The space group $C2/n$ was used for further refinement, with greatly improved correlation coefficients. Refinement led to the final R factors for 190 variables: R_1 $(=\sum||F_o| - |F_c||/\sum|F_o|)$ for $F_o^2 > 3\sigma(F_o)^2 = 0.081$ and $R_2 = 0.087$ for the complete data set. The goodness of fit was 0.84, and the final difference Fourier had a highest peak of 0.56 e/Å^3.

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0002-7863/82/1504-4298$01.25/0