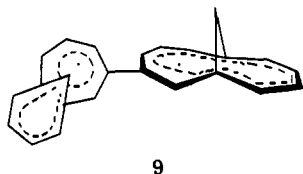
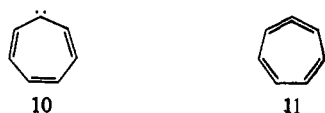


Jacobs, McLennon, and Muscio⁹ that perpendicular diallyl diradicals close to dimethylenecyclobutanes in a symmetry allowed conrotatory sense. Analogously, if it is assumed that orbital symmetry dictates the stereochemistry of the cyclobutane hydrogens in the reactions under discussion, diradicals **9** and its 180° rotomer be-



come viable precursors to **4a** and **4b**, respectively.¹⁰ Reasonable progenitors of **9** and its rotomer are the two diastereomeric allenes, **8**. Dimerization of either (allowed conrotatory) or both (allowed disrotatory) would give diradical(s) **9**, which, as mentioned above, could close in an allowed conrotatory sense to give the observed product.¹⁰ In support of **8** as a reasonable intermediate, recent INDO calculations¹¹ on cycloheptatrienyldiene (**10**) and cycloheptatetraene¹² (**11**)



place the bent, twisted allene at lower energy than the carbene. Since the chemistry of the seven-membered system^{5,13} is more consistent with a carbene as the reactive intermediate, this surprising result suggests the possibility of equilibria between aromatic carbenes and their allene forms. Furthermore, such equilibria would be sensitive to ring size. Thus, whereas cyclopropylidene (**12**) would exist only as the carbene, in the



larger rings it is quite possible that such equilibria would not only exist but would be shifted far enough to the allene side to show some or exclusive allene chemistry.¹⁴

(9) T. L. Jacobs, J. R. McLennon, and O. J. Muscio, Jr., *J. Amer. Chem. Soc.*, **91**, 6038 (1969); see also J. E. Baldwin and R. A. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970).

(10) The obvious drawback to this suggestion is that only one of the two possible products (**4a** or **4b**) is actually observed. This could be due either to interconversion of the diradicals to give one thermodynamically favored product or instability of one product to reaction or work-up conditions or, possibly, both. Perhaps it is worth noting that substantial amounts of intractable tars are invariably noted in these reactions and, in fact, even the isolated products are rather unstable. With regard to possible interconversion of the two radicals, it should be noted that, in order for them to interconvert, they must pass through **6** (anti) or **7** (syn). Thus, such an isomerization would require breaking the central fulvalene double bond under the reaction conditions. This of course, also introduces the possibility that **4** and **5** arise from sequences such as **1** → **6** → **9** → **4**. As a sole source of **4**, this appears unlikely since at low temperature (-35°) photolysis of **3** also gives **4**.

(11) R. L. Tyner, W. M. Jones, N. Y. Ohrn, and J. R. Sabin, *J. Amer. Chem. Soc.*, submitted for publication.

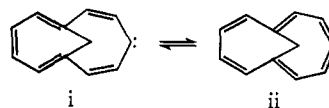
(12) This form was first suggested by K. Untch of Syntex Corporation, at the International Symposium on the Chemistry of Non-Benzenoid Aromatic Compounds, Sendai, Japan, Aug 1970.

(13) Cf. E. E. Waali and W. M. Jones, *J. Amer. Chem. Soc.*, **95**, 8114 (1973), and references cited.

(14) Although such an equilibrium between **1** and **8** may well be expected to lie further toward the allene structure than in the smaller seven-membered ring, ring size alone cannot be the whole picture since

Acknowledgment. The authors gratefully acknowledge the support of this work received from the National Science Foundation. Helpful discussions with Professor John Baldwin are also acknowledged.

the chemistry of $i \rightleftharpoons ii$ is that expected of an aromatic carbene.⁶ If such



equilibria exist, the differences in the chemistry of $1 \rightleftharpoons 8$ and $i \rightleftharpoons ii$ may be due to a trivial but difficult to discern (from models) difference in steric requirements of the two allenes or perhaps differences in the π -electron systems. In both cases, $i \rightleftharpoons ii$ and $1 \rightleftharpoons 8$, the chemistry observed is best explained in terms of the intermediate (**i** and **8**) which contains a homobenzenoid component in the π -electron system.

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Received September 25, 1973

Structural Characterization of Tris(pyrrolyldithiocarbamato)iron(IV) Perchlorate. An FeS₆ Complex of Unusually High Oxidation State

Sir:

Electrochemical and synthetic studies by ourselves^{1,2} and others³⁻¹³ have established that the dithiocarbamate ligand is extremely effective in stabilizing unusually high oxidation states of the first-row transition metals. X-Ray structural confirmation is now available for the two compounds Cu(R₂dtc)Br₂⁵ and [Ni(R₂dtc)₃]Br^{14,15} where the high oxidation states Cu(III) and Ni(IV) have been stabilized by the R₂dtc = *N,N*-di-*n*-butyldithiocarbamate ligand. The crystal structure of the Ni(IV) selenium analog [Ni(Se₂CN(C₄H₉)₂)₃]Br has also been determined.⁷

Iron(IV) complexes are rare.¹⁰ Despite the fact that [Fe(R₂dtc)₃]BF₄ with R₂ = Me₂, Et₂, *i*-Pr₂, pyr, and *c*-Hex₂ were synthesized more than 2 years ago,¹⁰ no structural confirmation of stereochemistry and oxidation state has been reported. We have therefore undertaken a single-crystal structure analysis of [Fe(R₂dtc)₃]ClO₄ with a view to elucidating the detailed coordination geometry of the FeS₆-core and comparing it with that of other metals in high oxidation states.

(1) R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Aust. J. Chem.*, **26**, 2533 (1973).

(2) A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, in press.

(3) H. C. Brinkhoff, J. A. Cras, J. J. Steggerda, and J. Willemsse, *Recl. Trav. Chim. Pays-Bas*, **88**, 633 (1969).

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(6) J. Willemsse, P. H. F. M. Rouwette, and J. A. Cras, *Inorg. Nucl. Chem. Lett.*, **8**, 389 (1972).

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(8) R. M. Golding, C. M. Harris, K. J. Jessop, and W. C. Tennant, *Aust. J. Chem.*, **25**, 2567 (1972).

(9) H. C. Brinkhoff, *Recl. Trav. Chim. Pays-Bas*, **90**, 377 (1971).

(10) E. A. Pasek and D. K. Straub, *Inorg. Chem.*, **11**, 259 (1972).

(11) H. C. Brinkhoff, A. M. Grotens, and J. J. Steggerda, *Recl. Trav. Chim. Pays-Bas*, **89**, 11 (1970).

(12) P. J. Beurskens, H. J. A. Blaauw, J. A. Cras, and J. J. Steggerda, *Inorg. Chem.*, **7**, 805 (1968).

(13) J. Willemsse and J. A. Cras, *Recl. Trav. Chim. Pays-Bas*, **91**, 1309 (1972).

(14) A. Avdeef, J. P. Fackler, and R. G. Fischer, *J. Amer. Chem. Soc.*, **92**, 6972 (1970).

(15) J. P. Fackler, A. Avdeef, and R. G. Fischer, *J. Amer. Chem. Soc.*, **95**, 774 (1973).

Table I. Structural Data for Some Metal Dithiocarbamates

Compound	Fe-S	S-S ^c	C-S	C-N	2θ ^d (deg)	Predominant ground state	Ref
[Fe(pyrr(dtc)) ₃]ClO ₄	2.300(2)	2.811(3)	1.714(6)	1.32(2)	38	³ T ₁	This work
Fe(pyrr(dtc)) ₃	2.41(1)	2.91(1)	1.70(3)	1.31(4)	39	⁶ A ₁	18b
Fe(<i>n</i> -Bu ₂ dtc) ₃	2.418(6)	2.86	1.70(2)	1.41(3)	33	⁶ A ₁	17
Fe(Et ₂ dtc) ₃ ^a	2.357(3)	2.846(3)	1.71(1)	1.33(1)	38	⁶ A ₁	19
Fe(Et ₂ dtc) ₃ ^b	2.306(1)	2.836(2)	1.721(4)	1.323(6)	40	² T ₂	19
Fe(Me, φdtc) ₃	2.32(1)	2.82(1)	1.68(3)	1.37(3)	40	² T ₂	18b
[Ni(<i>n</i> -Bu ₂ dtc) ₃]Br	2.261(1)	2.794(2)	1.708(5)	1.318(8)	45	¹ A ₁	15

^a Structure determined at 297°K. ^b Structure determined at 79°K. ^c Intraligand "bite." ^d Values calculated from an expression derived in ref 18 (octahedron 2θ = 60°, trigonal prism 2θ = 0°).

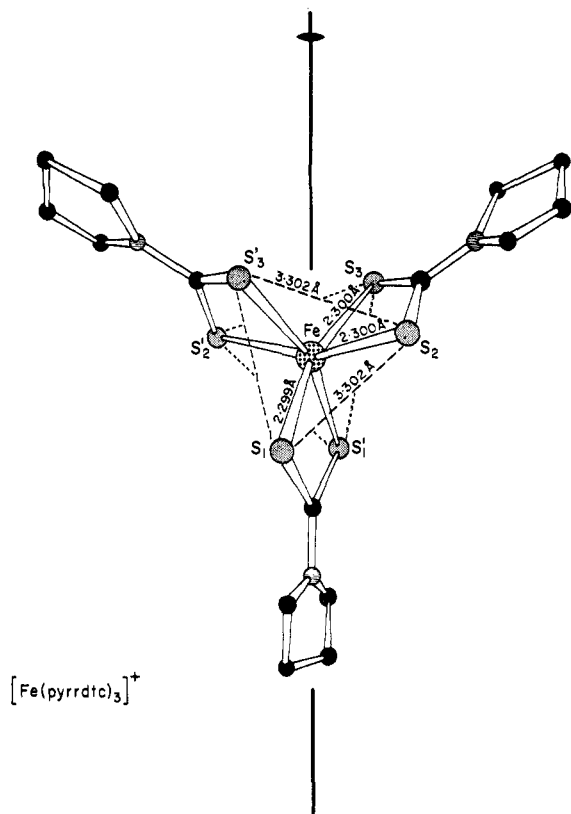
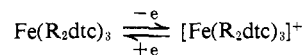


Figure 1.

We have selected the pyrrolidyl ($R_2 = (\text{CH}_2)_3$) derivative so that a direct comparison may be made with the known structure of the corresponding iron(III) compound.

Perhaps the most unexpected feature of these chelates is the relative ease of their preparation and their subsequent stability. The oxidation potential in acetone for the reversible couple



is only +0.41 V for $R_2 = \text{c-Hex}_2$ and +0.61 V for $R_2 = \text{pyrrolidyl}$.¹ In this work $[\text{Fe}(\text{pyrr}(\text{dtc}))_3]^+$ was prepared by aerial oxidation as a tetrafluoroborate salt using a 40% BF_3 , Et_2O solution in place of gaseous boron trifluoride as described by Pasek and Straub,¹⁰ and as the perchlorate salt by employing $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ as described by Golding, *et al.*⁸ Recrystallization of the crude solids by slow evaporation of nitromethane solutions yielded black cuboid crystals of each salt, the perchlorate being the more suitable for the

present X-ray studies. Crystal data: $\text{C}_{15}\text{H}_{24}\text{N}_3\text{S}_6\text{FeClO}_4$; $M = 594.07$ amu; monoclinic; $a = 17.049$, $b = 11.440$, $c = 12.639$ Å; $\beta = 97.72^\circ$; $D_{\text{measd}} = 1.60$, $D_{\text{calcd}} = 1.61$ g cm^{-3} for $Z = 4$; space group $I2/a$ (non-standard setting of $C2/c$); equivalent positions $(0, 0, 0; 1/2, 1/2, 1/2)(x, y, z), (\bar{x}, \bar{y}, \bar{z}), (1/2 + x, \bar{y}, z), (1/2 - x, y, \bar{z})$. Intensity data were collected with a Picker FACS-1 diffractometer using graphite crystal monochromated $\text{Cu K}\alpha$ radiation. A total of 1547 independent reflections with $I/\sigma(I) \geq 3.0$ were used to solve the structure *via* the conventional Patterson-Fourier methods. Least-squares refinement of nonhydrogen atoms yielded an R factor of 0.06. The perchlorate group occupies a site of $\bar{1}(C_1)$ symmetry at $(0, 0, 1/2)$ and its oxygen atoms are necessarily disordered.

The molecular structure of the $[\text{Fe}(\text{pyrr}(\text{dtc}))_3]^+$ cation is shown in Figure 1. The cation has exact C_2 symmetry with the Fe atom located at $(0.25, 0.0001, 0)$. The dithiocarbamate ligands are related by the twofold symmetry of the complex with the unique ligand being bisected by the C_2 axis. Structurally the coordination geometry of $[\text{Fe}(\text{pyrr}(\text{dtc}))_3]^+$ is very similar (*cf.* Table I) to that of the iron(III) derivative $[\text{Fe}(\text{pyrr}(\text{dtc}))_3]$. The average Fe-S distance in the low-spin¹⁰ Fe(IV) complex is significantly shorter (0.11 Å) than in the high-spin¹⁶ Fe(III) *n*-butyl¹⁷ and pyrrolidyl¹⁸ complexes. This is consistent with depopulation of antibonding e_g orbitals, *viz.*, $\text{Fe}^{\text{III}}(t_2^3e^2) \rightarrow \text{Fe}^{\text{IV}}(t_2^4)$, and the increased oxidation state of the central iron atom. The latter contribution to the shortening appears to be minimal since similar Fe-S bond lengths are observed for low-spin^{18,19} Fe^{III} (t_2^5) and the present Fe^{IV} (t_2^4) dithiocarbamates.

The FeS_6 core conforms neither to the ideal octahedral nor trigonal prismatic arrangement. Rather the angular twist 2θ between the triangular faces ($S_1-S_2-S_3'$) and ($S_1'S_2'S_3$) adopts a value of 38° intermediate between the extremes of 60 and 0° for the limiting configurations of higher symmetry. The structural data summarized in Table I for Fe(III), Fe(IV), and Ni(IV) dithiocarbamates reveal that, apart from M-S distances, the dimensions are generally closely similar. The absence of structural or electrochemical¹ anomalies implies that the evidence is unequivocal for describing $[\text{Fe}(\text{pyrr}(\text{dtc}))_3]\text{ClO}_4$ in the conventional terms of three formally uninegative dithiocarbamate ligands and a

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central iron atom stabilized in an unusually high (+4) oxidation state.

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 Received February 8, 1974

CIDNP in Dispiro[2.2.2]deca-4,9-diene in Its Thermolysis. CIDNP Derived from a Short-Chain Singlet Biradical

Sir:

The phenomenon of CIDNP has been successfully accounted for by the radical pair theory proposed by Closs¹ and by Kaptein and Oosterhoff.²⁻⁵ According to this theory, to observe CIDNP it is necessary that a radical pair separates after its birth to a distance where the S-T₀ splitting in the pair is sufficiently small and spends a sufficiently long time at that distance to allow substantial S-T₀ mixing by hyperfine interactions and g shift. In normal radical pairs, the above condition is easily fulfilled by diffusive displacements of the components.⁶ In biradicals, however, radical centers cannot be separated beyond the distance the molecular structure allows. Therefore, such a requirement can be a severe limitation to the observation of (S-T₀) CIDNP in the reactions of short-chain biradicals and, to our knowledge, (S-T₀) CIDNP has not been observed in the products derived from these species. We report here the observation of CIDNP effect in a product which seems certain to be derived from a short-chain singlet biradical.

The nmr spectrum of dispiro[2.2.2]deca-4,9-diene (**1**) consists of two sharp singlets at δ 0.6 and 4.8.⁷ An nmr tube containing the solution of **1** in triglyme was placed in the probe of a JEOL PS-100 spectrometer preheated at 193° and the spectrum was recorded repeatedly. After an initial period of time for the sample to warm up, the intensity of the singlet at δ 0.6 began to increase rapidly and reached a maximum⁸ after ca. 150 sec, while that of the singlet at δ 4.8 decreased and the signal turned to emission after ca. 70 sec (Figure 1). During the decomposition of **1**, CIDNP signals which would be due to the reaction products⁹ were also observed.^{10,11} The polarization in **1** was observed in *p*-di-

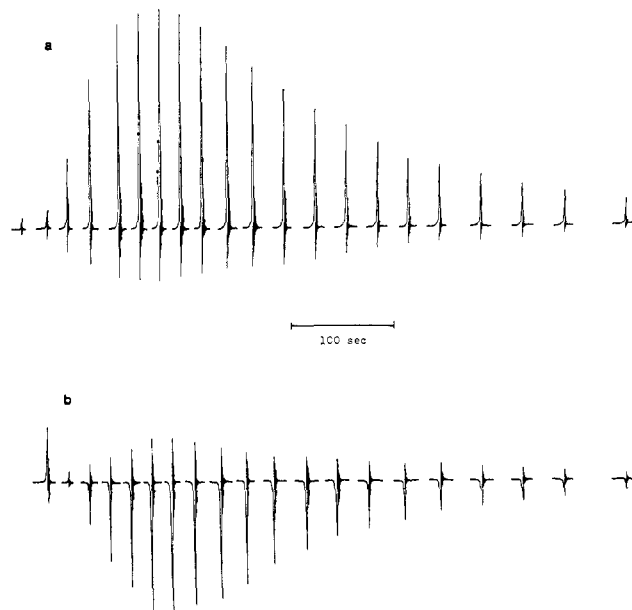
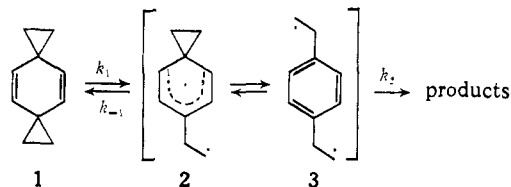


Figure 1. Time development of the polarization during decomposition of dispiro[2.2.2]deca-4,9-diene in triglyme at 193°, obtained by repeated sweeping through regions of δ 0.6 (a) and 4.8 (b). The spectrum amplitude of (b) is ten times that of (a).

bromobenzene and diphenyl ether as well as in triglyme.

The rate of disappearance of **1** ($4.53 \times 10^{-3} \text{ sec}^{-1}$ at 193° in triglyme) was in good agreement with that of the decay of the polarized signals, and maximum intensity of the enhanced absorption at δ 0.6 was found to depend linearly on the concentration of **1** ranging from 0.01 to 0.1 M. These results clearly showed that the responsible species for the polarization in **1** was formed in a first-order reaction from **1**. The first step of the reaction would no doubt be homolytic cleavage of the cyclopropane ring. The resulting biradical, **2**,



would further rearrange to **3** because **2** was structurally equivalent to the intermediate postulated in 1,2-aryl migration.¹²⁻¹⁶ In the presence of radical scavenger

(12) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

(13) The possibility that **3** underwent further rearrangement to **4** will



be slight, though it cannot be ruled out rigorously. Although the allyl-carbinyl-cyclopropylcarbinyl radical rearrangement, to which $2 \rightleftharpoons 3$ corresponds, is the well-documented process,¹⁴⁻¹⁶ few, if any, instances of the allylcarbinyl-cyclobutyl radical rearrangement have been known. We have obtained no experimental results which indicated the intermediacy of **4**.

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(6) F. J. Adrian, *J. Chem. Phys.*, **54**, 3912 (1971).

(7) T. Tsuji, S. Nishida, and H. Tsubomura, *J. Chem. Soc., Chem. Commun.*, 284 (1972).

(8) The maximum enhancement factor $I_{\text{max}} - I_0/I_0$, where I_{max} was the maximum intensity and I_0 , the thermal equilibrium intensity, was ca. 20.

(9) The thermolysis of **1** in diglyme afforded *p*-diethylbenzene in 73% yield.

(10) An enhanced triplet absorption at δ 1.2, an enhanced quartet absorption at δ 2.5, and a sharp singlet emission at δ 7.0.

(11) Samples were deoxygenated by argon bubbling. One of the samples was degassed through four freeze-thaw cycles on a vacuum line (1×10^{-3} mm).