Table I. Melting Points and Spectral Data of **2a–d**

product	mp, °C	IR (KBr), cm⁻¹	¹H NMR (CDCl₃), δ	UV (hexane) λ_{max}, nm
2a	199.5–200.0 dec	2950, 1460, 1370, 1160	1.34 (s, 36 H)	255 (log ε 4.29), 305 (4.07), 506 (4.23)
2b	110.0–110.5 dec	2950, 1455, 1363, 1240, 1160	2.97 (q, 4 H, CH_2CH₃), 1.33 (s, 18 H, *t*-Bu), 1.32 (t, 6 H, CH₂CH_3)	258 (4.26), 303 (3.96), 515 (4.11)
2c	158.0–158.5 dec	2950, 1370, 1245, 1160	2.54 (s, 6 H, Me), 1.32 (s, 18 H, *t*-Bu)	259 (4.24), 304 (3.91), 534 (4.03)
2d	116.5–117.0 dec	2950, 1460, 1380, 1230, 1150, 1045	3.40 (sep, 4 H, CHMe₂), 1.26 (d, 24 H, Me)	258 (4.30), 301 (3.95), 505 (4.13)
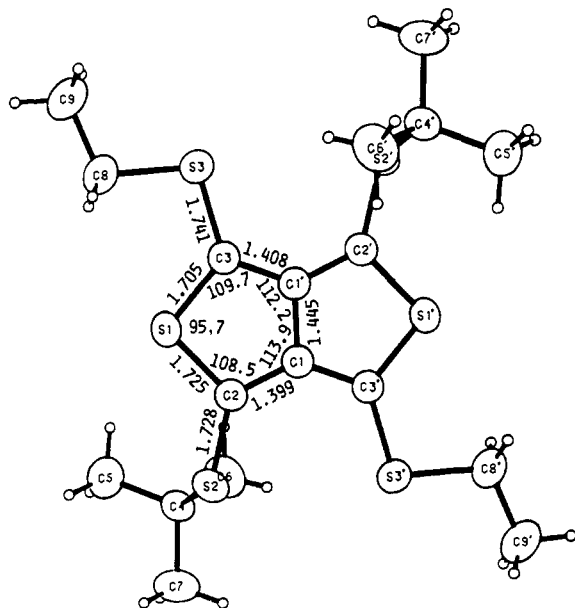
Figure 1. Molecular structure of **2b** with selected bond distances and angles. The estimated standard deviations are 0.002–0.003 Å for distances and 0.1–0.2° for angles.

for 4 h under nitrogen. The solvent was evaporated and the dark red residue was recrystallized from benzene–hexane to give **2a** as reddish purple crystals in 40% yield. Similarly, thieno[3,4-*c*]thiophenes **2b**, **2c**, and **2d** were prepared from cyclopropenethiones **1b**, **1c**, and **1d**, in 26%, 12%, and 38% yields, respectively. One reason for the poor isolated yields of **2a–d** (especially **2c**) is that they decompose slowly on exposure to air in the purification procedure. Potts and his co-workers[3d] have reported the ready addition of oxygen to 1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene followed by decomposition. In our attempt to prepare 1,3,4,6-tetrakis(ethylthio)thieno[3,4-*c*]thiophene (**2e**) from 2,3-bis-(ethylthio)cyclopropenethione (**1e**) under similar conditions, the reaction solution turned dark red and showed the characteristic visible absorption at 507 nm suggesting the formation of **2e**, but the product could not be isolated owing to rapid blackening in the air. The result clearly indicates that the less bulky ethylthio groups are unable to hinder the addition of oxygen at 1,3,4,6-positions of the thieno[3,4-*c*]thiophene. Purified thieno[3,4-*c*]-thiophenes, **2a–d**, are stable for long periods at room temperature in the air. The melting points and spectral data are summarized in Table I.

The cycloaddition reactions of **2a** and **2d** with dimethyl acetylenedicarboxylate in refluxing xylene were examined. The former gave no cycloadduct, while the latter 5,6-dicarbomethoxybenzo-[*c*]thiophene (**3**) formed by extrusion of sulfur from the initial

2d   R = i-Pr   3

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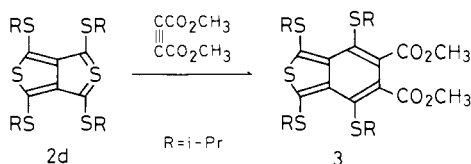
(5) Cyclopropenethiones **1a–e** were prepared according to the method of Weiss, Schlierf, and Schloter.[6]

(6) Weiss, R.; Schlierf, C.; Schloter, K. *J. Am. Chem. Soc.* **1976**, *98*, 4668.

1:1 cycloadduct in 29% yield. The structural assignment of **3** was established by the IR, ¹H NMR, and mass spectra.[7] The failure of **2a** to undergo cycloaddition could be attributed to the steric protection provided by the *tert*-butylthio groups.

The crystals of **2b** suitable for an x-ray structure determination were obtained from ethanol. Crystal data: **2b**, C₁₈H₂₈S₆, triclinic, space group P$\bar{1}$, a = 10.229 (1) Å, b = 10.870 (1) Å, c = 5.790 (1) Å, α = 102.00 (1)°, β = 103.20 (1)°, γ = 60.74 (1)°, Z = 1. The structure was solved by direct methods and refined by full-matrix least squares to final R value of 0.026. Figure 1 shows the molecular structure of **2b** with selected bond distances and angles.

Supplementary Material Available: Tables of general temperature factor expressions and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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(7) Data for compound **3**: mp 95.5–96.0 °C; IR (KBr) 2950, 1740, 1440, 1380, 1280, 1245, 1200, 1165 cm⁻¹; ¹H NMR (CDCl₃) δ 3.92 (s, 6 H), 3.43 (sep, 2 H), 3.32 (sep, 2 H), 1.27 (d, 12 H), 1.17 (d, 12 H); MS, *m/e* 546 (M⁺).

Pressure-Induced Torsional Isomerism in [*n*-Bu₄N]₂[Re₂X₈] (X = Br, I)

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The structural hallmark of the metal–metal quadruple bond, first characterized in [Re₂Cl₈²⁻],[1] is an eclipsed conformation of the two ML₄ halves of the molecule, despite the resulting steric interactions.[2] Twisted conformations, however, can be induced in certain cases by ligands bridging the two metal centers.[3] We wish to report evidence that high pressure applied to salts of both [Re₂I₈²⁻] and [Re₂Br₈²⁻] causes torsion from an eclipsed to a staggered conformation.

Crystals of [*n*-Bu₄N]₂[Re₂I₈][4] were suspended in a dispersed poly(methyl methacrylate)/dichloromethane medium, which was then evaporated, and a piece of the resulting film was placed under static pressure in a diamond anvil cell.[5] With increasing pressure a new band appears in the visible spectrum (see Figure 1), red-shifted from the well-known ¹(δ²) → ¹(δδ*) transition of the eclipsed form.[2] Analogous behavior is observed for [*n*-Bu₄N]₂-

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(1) (a) Cotton, F. A., et al. *Science (Washington, D.C.)* **1964**, *145*, 1305. (b) Cotton, F. A. *Inorg. Chem.* **1965**, *4*, 334. (c) Cotton, F. A.; Harris, C. B. *Inorg. Chem.* **1965**, *4*, 330.

(2) Cotton, F. A.; Walton, R. A. "Multiple Bonds between Metal Atoms"; Wiley: New York, 1982.

(3) Campbell, F. L., III; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1984**, *23*, 4222 and references therein.

(4) Preetz, W.; Rudzik, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 150.

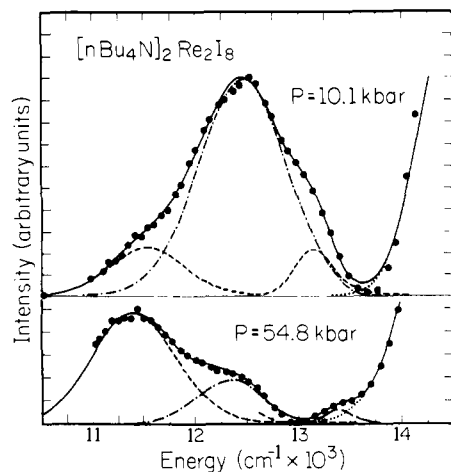(5) Jurgensen, C. W.; Drickamer, H. G. *Phys. Rev. B* **1984**, *30*, 7202.

Communications to the Editor

J. Am. Chem. Soc., Vol. 107, No. 20, 1985 5803

Figure 1. Low-energy spectra of $[n\text{-Bu}_4\text{N}]_2[\text{Re}_2\text{I}_8]$ at 10.1 and 54.8 kbars. The dashed and dotted curves represent a Gaussian deconvolution of the spectrum. The solid line is the summation of the individual Gaussian peaks and shows the accuracy of the fit. The lowest energy peak is the pressure-induced peak. The intermediate-energy peak is the $^1(\delta^2) \rightarrow {}^1(\delta\delta^*)$ excitation of the eclipsed form. The small peak at slightly higher energies is either a $\pi \rightarrow \delta^*$ or $\delta \rightarrow \pi^*$ excitation; its behavior will be discussed in ref 18.

$[\text{Re}_2\text{Br}_8]$,[6] except that the spectral changes with increasing pressure are less dramatic.

The new, low-energy peak appears at ca. 11 500 cm^{-1} for the iodide and at ca. 12 100 cm^{-1} for the bromide. In each case the transition is assigned as $^1(\delta^2) \rightarrow {}^1(\delta\delta^*)$ for the staggered conformer. These transition energies are consistent with the value (11 800 cm^{-1}) estimated for a fully staggered form of $\text{Mo}_2\text{X}_4(\text{L}-\text{L})$.[7] Furthermore, these results are easily understood in terms of an emerging experimental[8-10] and theoretical[11,12] picture of the $^3(\delta\delta^*)$ and $^1(\delta\delta^*)$ excited states for metal–metal quadruple bonds. The energy difference between the $^1(\delta)^2$ ground state and the $^3(\delta\delta^*)$ excited state is largely dependent on the $d_{xy}-d_{xy}$ overlap integral, which is small (ca. 0.1) in the eclipsed form and vanishes in the fully staggered form. On the other hand the separation between the $^3(\delta\delta^*)$ and $^1(\delta\delta^*)$ states is determined by the relatively large electron–electron repulsion in the ionic singlet state, and this term does not depend significantly on the twist angle. The closely similar transition energies observed for the staggered or nearly staggered conformations in these dirhenium and dimolybdenum complexes suggests that the electron repulsion term is also relatively insensitive to the identity of the metals or ancillary ligands. More examples are needed to test this idea.[13] Nevertheless, since the $^1(\delta^2)$ and $^3(\delta\delta^*)$ states should be nearly degenerate in the staggered form, the red-shift of the $^1(\delta^2) \rightarrow {}^1(\delta\delta^*)$ transition for this form provides a measure (presumably a lower limit) of the $^1(\delta^2)$ and $^3(\delta\delta^*)$ separation in the eclipsed form.[9] In the present
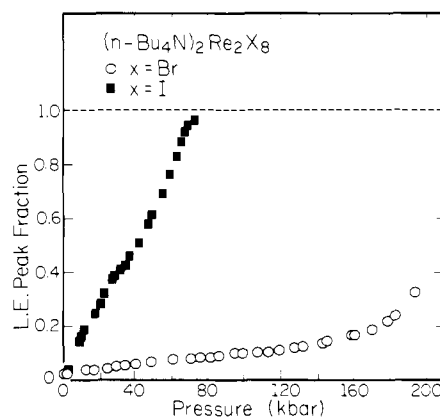

Figure 2. Area fraction of absorption intensity under the low-energy peak representing the staggered conformation vs. pressure for $[n\text{-Bu}_4\text{N}]_2$-$[\text{Re}_2\text{X}_8](\text{X}=\text{Br,I})$.

case these values are ca. 1100 cm^{-1} for the iodide and ca. 1800 cm^{-1} for the bromide. For comparison, values of ca. 3200–3600 cm^{-1} are predicted for the singlet–triplet separation in the analogous chloride from recent calculations.[11,12]

In Figure 2 we present the relative areas of the two singlet transitions as a function of pressure for both the iodide and the bromide. The fractional area associated with the lower energy peak approaches unity at ca. 80 kbar for the iodide but is only ca. 0.2 at 180 kbar for the bromide. These spectral changes are totally reversible; upon diminishing the pressure, no hysteresis with respect to peak locations or intensities is observed.

To convert the data in Figure 2 to mole fractions and extract equilibrium constants requires that we know transition moments for both excitations. Since the total intensity under the peaks for the iodide decreases by a factor of ca. 3 from 1 atm to 70 kbars, this correction is not trivial. However, from eq 1 we can extract

$$[\partial \ln K / \partial P]_T = - (\Delta V / RT) \tag{1}$$

the volume change on isomerization, if we assume the ratio of transition moments is independent of pressure. These results are for the iodide, 2.2 cm^3/mol, and for the bromide, 0.25 cm^3/mol. The accuracy for the iodide is $\pm 10\%$ and for the bromide ± 10–15%. In either case this constitutes a very small fraction of the molar volume. Despite the expected $\text{X} \cdots \text{X}$ nonbonded repulsions, the rhenium–rhenium bond distance in $[\text{Re}_2\text{Br}_8{}^{2-}]$ (2.228 Å)[16] is not significantly different from that in $[\text{Re}_2\text{Cl}_8{}^{2-}]$ (2.222 Å).[17] In contrast, the quadruple bond distance in $[\text{Re}_2\text{I}_8{}^{2-}]$ has been estimated as 2.27 Å.[4] The significantly larger volume change observed for the iodide presumably reflects the relatively enhanced steric interactions in its eclipsed form, resulting in greater relaxation upon twisting to the staggered form.

A complete account and discussion of the shifts with pressure of the $\delta-\delta^*$, $\pi-\pi^*$, and charge-transfer excitations of $[\text{Re}_2\text{X}_8{}^{2-}]$ (X = Cl, Br, I) will be presented elsewhere.[18]

(6) Cotton, F. A.; Curtis, N. F.; Robinson, W. R. *Inorg. Chem.* **1965,** *4,* 1696.

(7) Campbell, F. L., III; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1985,** *24,* 177.

(8) Miskowski, V. M.; Goldbeck, R. A.; Kligar, D. S.; Gray, H. B. *Inorg. Chem.* **1979,** *18,* 86.

(9) Hopkins, M. D.; Zietlow, T. C.; Miskowski, V. M.; Gray, H. B. *J. Am. Chem. Soc.* **1985,** *107,* 510.

(10) Zietlow, T. C.; Hopkins, M. C.; Gray, H. B. *J. Solid State Chem.* **1985,** *57,* 112.

(11) Hay, P. J. *J. Am. Chem. Soc.* **1982,** *104,* 7007.

(12) Bursten, B. E.; Cotton, F. A.; Fanwick, P. E.; Stanley, G. G. *J. Am. Chem. Soc.* **1983,** *105,* 3082.

(13) Two recent studies of *carboxylate*-bridged dimers (necessarily eclipsed) have assigned much larger energies for the $^1(\delta^2)-{}^3(\delta\delta^*)$ separation, i.e., 16 500 cm^{-1} for $\text{Re}_2[\text{O}_2\text{CCMe}_3]_4\text{Cl}_2$[14] and 14 500 cm^{-1} for $\text{W}_2[\text{O}_2\text{CCF}_3]_4$.[15] Thus, carboxylate ligands may be more intimately involved than halide or phosphine ligands in determining the excited-state energies.

(14) Martin, D. S.; Huang, H.-W.; Newman, R. A. *Inorg. Chem.* **1984,** *23,* 699.

(15) Santure, D. J.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1985,** *24,* 371.

(16) Cotton, F. A.; DeBoer, B. G.; Jeremic, M. *Inorg. Chem.* **1970,** *9,* 2143.

(17) Cotton, F. A.; Frenz, B. A.; Stults, B. R.; Webb, T. R. *J. Am. Chem. Soc.* **1976,** *98,* 2768.

(18) Carroll, T. L.; Shapley, J. R.; Drickamer, H. G. *J. Chem. Phys.,* manuscript in preparation.