most importantly, the National Institutes of Health (Grant AI-07869) for financial support.

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The Structure of Di-π-cyclooctatetraeneuranium (Uranocene)

Sir:

Streitwieser and Mueller-Westerhoff have recently reported the synthesis and characterization of bis(cyclooctatetraene)uranium.[1] As the name "uranocene" implies, this compound was proposed to be a new type of sandwich metal complex homologous with ferrocene.[2] We have completed an X-ray diffraction analysis of a single crystal of this material which shows it is indeed a π sandwich compound with a molecular symmetry of D_{8h} as shown in Figure 1.

The deep green compound crystallizes in $P2_1/n$ (an alternate setting of $P2_1/c$, C_{2h}^5) with $a = 7.084\ (3)$,[3] $b = 8.701\ (3)$, $c = 10.631\ (5)$ Å, $\beta = 98.75°\ (3)$, $V = 6476\ (10)$ Å^3. For two formula units in the cell, the calculated density of 2.29 g/cm^3 is in the range expected from comparison with heavy metal compounds which have similar formulas. Several of the extremely air-sensitive crystals were sealed within thin-walled quartz capillaries (0.3 mm in diameter) under a carefully purified nitrogen atmosphere. Intensity data were collected by the stationary crystal–stationary counter method on a manually operated diffractometer using Zr-filtered Mo $K\alpha$ radiation out to a Bragg 2θ angle of 35°. These data were corrected for absorption.

With two formula units in the cell the molecule may be unambiguously placed on the origin with $\bar{1}$ (C_i) crystallographic point symmetry. The uranium atoms then contribute only to structure factors $F(h,k,l)$ for which $h + k + l$ is even. Those structure factors with $h + k + l$ odd are due entirely to the scattering of the carbon and hydrogen atoms. For this class of reflections the problem is virtually the same as a light-atom structure. Assignment of phases for these reflections is then difficult, but their magnitudes are very sensitive to the carbon atom positions.

Because of the enormous scattering power of the uranium atom, especially at large 2θ angles, a standard Patterson map was dominated by Fourier ripple peaks around the origin and no uranium–carbon vectors could be discerned. However, an origin-removed sharpened Patterson map showed very little ripple, and the strongest eight peaks in this map for vectors in the range 1.6–3.0 Å all had lengths of about 2.6 Å and clearly showed the sandwich structure of the molecule with virtually no significant distortion. The coordinates from the Patterson map were directly used in subsequent least-squares refinements. To test the correctness of the carbon atom positions, refinements were carried out both for the full data set and for the class with $h + k + l$ odd (which are in general weak but due *only* to the carbon and hydrogen scattering). The standard R factor, including all data with only the uranium atom included in the structure-factor calculations, is 10.8%. The standard R factor after refinement of the carbon atom positional parameters, using only the data with $h + k + l$ odd, is 11.4%. The present level of refinement for all 540 reflections with $F^2 > \sigma(F^2)$ corrected for absorption gives R and wt R as 3.3 and 3.9%, respectively. A difference Fourier shows no peaks greater than 0.9 e/Å^3. The largest of these peaks are either within 0.1 Å or so of the origin and due to uncorrected anisotropy in the uranium electron density, or are at positions corresponding to those calculated for hydrogen atoms.

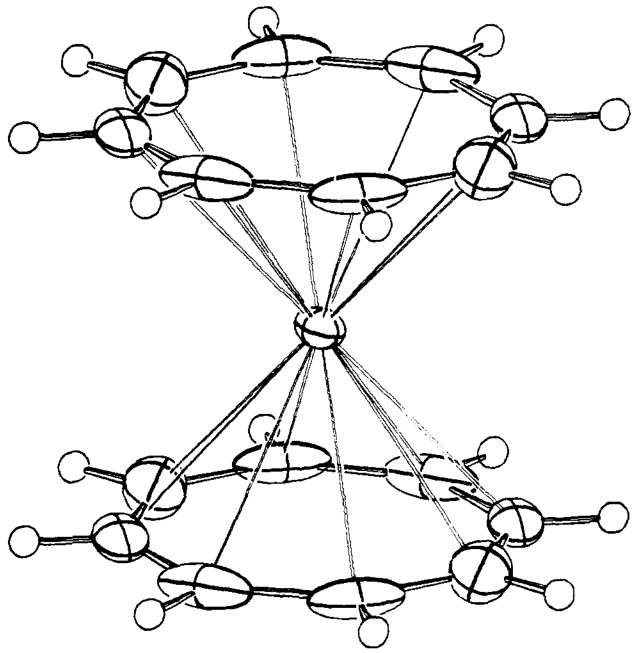

Figure 1. A perspective drawing of $(C_8H_8)_2U$, di-π-cyclooctatetraeneuranium.

Since the molecule lies on the origin with $\bar{1}$ (C_i) crystallographic point symmetry, the two planar C_8H_8 rings are then constrained to be parallel and eclipsed. The orientations of the carbon atom thermal ellipsoids (Figure 1) show a preferential oscillation of the rings about the molecular symmetry axis, as expected in a compound of this type. The rms amplitude of vibration along the major axis is approximately 0.35 Å for all of the carbon atoms in the ring. The U–C and C–C bond lengths are all equivalent to within the present level of refinement. The average U–C bond length is 2.648 (5) Å, with the assigned standard deviation estimated from the variance. The standard deviations of individual U–C and C–C bonds as determined from the variance–covariance matrix are 0.02 and 0.03 Å, respectively. The average C–C bond length is 1.395 (15) Å. The two averages for alternating sets of four bonds are 1.391 and 1.398 Å. The eight carbon atoms of an individual ring all lie within about 0.02 Å of the least-squares plane. This planarity and the equality of alternate bond lengths leave no question that this is a pseudoaromatic ring and that di-π-cyclooctatetraene-

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(1) A. Streitwieser and U. Mueller-Westerhoff, *J. Amer. Chem. Soc.*, **90**, 7364 (1968).

(2) Although other complexes of planar cyclooctatetraene dianion are known (see, for example, M. A. Bennett, *Advan. Organometal. Chem.*, **4**, 376 (1966); H. Breil and G. Wilke, *Angew. Chem. Intern. Ed. Engl.*, **5**, 899 (1968)), these compounds contain rather weakly bound C_8H_8 dianions and show chemical behavior characteristic of ionic bonding.

(3) The standard deviation in the least significant digits is given in parentheses.

uranium or "uranocene" is an authentic π sandwich complex of the 5f transition series.

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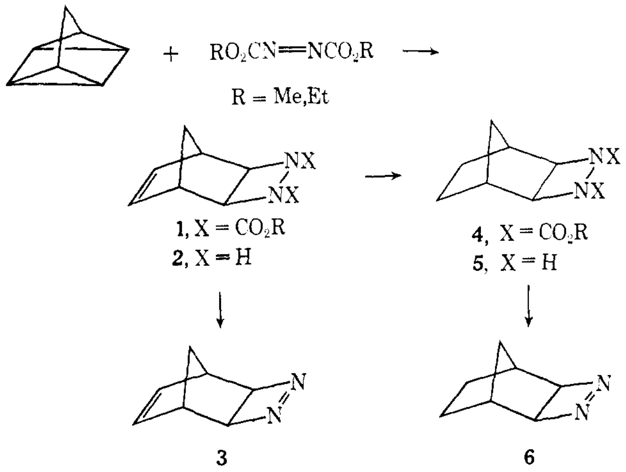
Δ^1-1,2-Diazetines

Sir:

We wish to report on the synthesis and decomposition of two four-membered-ring azo compounds (Δ^1-1,2-diazetines), **3** and **6**. Dimethyl and diethyl azodicarboxylate added readily to quadricyclane to give **1** (74%, R = Me).[1] Saponification and decarboxylation of **1** in methanolic potassium hydroxide yielded the hydrazine **2**, which was oxidized without isolation by cupric chloride to the Cu^{I} complex of the azo compound.[3] Aqueous alkali freed this Δ^1-1,2-diazetine (**3**, 36% from **1**, R = Et); it was purified by sublimation: mp 65–66°; ν_{max}^{KBr} 1558 cm^{-1} ($\nu_{N=N}$); nmr δ 1.03, 1.45, AB doublets, J = 10 Hz (C-9), 2.92, unresolved multiplet (C-1, C-6), 3.99, singlet, (C-2, C-5), 6.13, triplet, J = 1.7 Hz (C-7, C-8).[4] Hydrogenation of **1** over palladium–charcoal gave the saturated urethane **4**, which was transformed as above into Δ^1-1,2-diazetine **6** (31% from **1**, R = Me): mp 128.5–129.5° after three sublimations; ν_{max}^{KBr} 1550 cm^{-1} ($\nu_{N=N}$); nmr δ 0.83–1.72 (C-7, C-8), 1.23, broad singlet (C-9), 2.43, unresolved multiplet (C-1, C-6), 4.40, singlet (C-2, C-5).[4]



Norbornene and nitrogen were the only products detected in the thermal decomposition of **6** in solution or in the vapor phase. The kinetics were studied in the vapor phase (80–300 mm) at constant volume in an apparatus which monitored pressure continuously.

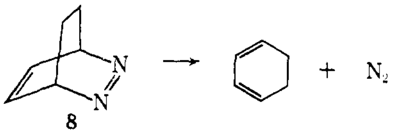
Table I

Compd	10^5k, sec^{-1}	Temp, °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
3	4.09 88.2	118.5 148.1	33.1 ± 0.5	5.4 ± 1
6	3.20 45.9	134.5 161.8	33.7 ± 0.5	3.0 ± 1
7			36.0 ± 0.2 36.4 ± 0.3	5.8 ± 0.5[a] 6.3 ± 0.5[b]

[a] R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, **88**, 3963 (1966). [b] S. G. Cohen, R. Zand, and C. Steel, *ibid.*, **83**, 2895 (1961).

Fragmentation was found to be first order, with the rates and activation parameters shown in Table I. Note that $\Delta H^{\ddagger}$ for decomposition of **6** is nearly as high as that for fragmentation of the bicyclic pyrazoline 2,3-diazanorbornene (**7**), even though the latter yields a high-energy intermediate, a 1,3 biradical.[5,6]

For comparison with the behavior of **6**, the decomposition of 2,3-diazabicyclo[2.2.2]octa-2,5-diene (**8**) to 1,3-cyclohexadiene and nitrogen was examined. The azo compound was generated by *t*-butyl hypochlorite oxidation of the corresponding hydrazine at −78°, and it fragmented rapidly at this temperature.[8,9] *Indeed, the decomposition of* **8** *is estimated to be* 10^{22} *times faster than that of* **6** *at* −78°. Clearly the key difference between the two reactions is the orbital-symmetry allowedness of the former (a retro-Diels–Alder) *vs.* the forbiddenness of the latter (a retro-2+2 cycloaddition).[10] Among other differences, the most significant is probably relief of strain in the four-membered ring, a factor which would tend to diminish, not heighten, the contrast in rates. Moreover, the influence of orbital-symmetry forbiddenness on rate may be attenuated for reactions having very large enthalpy changes (a consequence of the Hammond postulate); fragmentation of **6** is estimated to release *roughly 60 kcal/mol.*



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If one assumes for decomposition of **8** the value of $\Delta S^{\ddagger}$ (10.5 eu) found for its close relative 2,3-diazabicyclo[2.2.2]-2-octene,[11] the dramatic rate difference separating allowed and forbidden processes corresponds to $\delta\Delta H \simeq 18$ kcal/mol. Earlier estimates of the "energetic price of orbital-symmetry forbid-

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[1] Evidence for its configuration will be set forth in a full paper. The diethyl adduct has been prepared independently by C. D. Smith (personal communication), who discovered the addition of dienophiles to quadricyclane.[2]

[2] C. D. Smith, *J. Amer. Chem. Soc.*, **88**, 4273 (1966).

[3] O. Diels, J. H. Blom, and W. Koll, *Ann.*, **443**, 242 (1925).

[4] Relative peak areas were appropriate for these assignments, and elemental analysis confirmed the composition. Interestingly, the highest *m/e* fragment of appreciable intensity obtained at 70 eV corresponds to loss of N_2.

[5] E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **89**, 7134 (1967); see, however, W. R. Roth and J. Martin, *Ann.*, **702**, 1 (1967).

[6] The thermal stability of 3,3,4,4-tetrafluoro-Δ^1-1,2-diazetine is comparable.[7a] Nitrogen loss from the other previously known Δ^1-1,2-diazetine, a photoisomer from 9,9′-azoanthracene,[7b] would give a highly strained olefin;[7c] hence, it reverts at its melting point (284–287°) to its progenitor.

[7] (a) H. J. Emeléus and G. L. Hurst, *J. Chem. Soc.*, 3276 (1962); (b) D. E. Applequist, M. A. Lintner, and R. Searle, *J. Org. Chem.*, **33**, 254 (1968); (c) N. M. Weinshenker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968), and references therein.

[8] R. Askani oxidized the same hydrazine with mercuric oxide at −5 to −10° and noted that the azo compound immediately decomposed to diene and nitrogen (*Chem. Ber.*, **98**, 2551 (1965)).

[9] Very recently J. A. Berson and S. S. Olin generated *cis*- and *trans*-3,6-dimethyl-3,6-dihydropyridazine by oxidation of the corresponding hydrazine. The azo compounds decomposed too fast even at −50° to be detectable by uv spectroscopy (*J. Amer. Chem. Soc.*, **91**, 777 (1969)).

[10] (a) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965); (b) *Accounts Chem. Res.*, **1**, 15 (1968).

[11] S. G. Cohen and R. Zand, *J. Amer. Chem. Soc.*, **84**, 586 (1962).