the isolation of $Mo_2(O\text{-}i\text{-}Pr)_4(HO\text{-}i\text{-}Pr)_4$, though it is likely that this compound or a dimethylamine-substituted derivative is a reactive intermediate.[6,7]

$Mo_2(O\text{-}i\text{-}Pr)_4(dmpe)_2$ is a dark-brown, hydrocarbon-soluble, air-sensitive, crystalline compound.[8] The NMR spectra in toluene-d_8 revealed a single ^{31}P signal and only one type of O-*i*-Pr ligand with equivalent isopropyl–methyl groups.[9] A molecule having a staggered $Mo_2O_4(P\text{–}P)_2$ unit similar to that seen in $\beta\text{-}Mo_2Cl_4(dppe)_2$ should have displayed diastereotopic methyl groups. The NMR data are consistent with expectations based on the molecular structure found in the solid state.[10] See Figure 1. The dmpe ligands do not span the Mo–Mo bond but rather act as chelating ligands to *one* molybdenum atom. The four alkoxides are bonded to the other molybdenum atom. The $Mo_2O_4P_4$ unit adopts a staggered conformation as is evident from one of the views shown in Figure 1. This is the only example of an unsupported M–M multiple bond uniting Mo(0) and Mo(IV) atoms, though it should be recognized that M–M multiple bonds between metal atoms in different oxidation states have been known since the discovery of $Re_2Cl_5(C_4H_{10}S_2)_2$ in 1966 ($C_4H_{10}S_2$ is 2,5-dithiahexane).[11] The recent report of the Re(IV)–Re(II) dinuclear compound $Re_2(OEt)_2Cl_4(PPh_3)_2$ is particularly worthy of note in that the Re(IV) center is supported by two alkoxide ligands.[12]

We propose that the M–M multiple bond in this molecule is a triple bond, $\sigma^2\pi^4$, uniting the d^2 Mo(IV) and d^6 Mo(O) metal atoms.[13] This is consistent with the observed Mo–Mo distance which is comparable to those in $Mo_2(OR)_6L_2$ compounds,[14] e.g., Mo–Mo = 2.242 (1) Å in $Mo_2(OSiMe_3)_6(HNMe_2)_2$.[15] Formation of a δ bond can be ruled out based on the staggered $Mo_2O_4P_4$ conformation, and the Mo(0) center will have two electrons residing in a metal-centered atomic orbital, namely, the d_{xy} orbital which otherwise could be involved in δ bonding. At the $Mo(O\text{-}i\text{-}Pr)_4$ center, the metal d_{xy} orbital is involved in Mo–O π bonding.[16]

Though we cannot rule out the possibility that the title compound represents a kinetic rather than the thermodynamic product of reaction 1, this seems unlikely. Why should a molecule of formula $Mo_2(O\text{-}i\text{-}Pr)_4(dmpe)_2$ favor the observed Mo(IV)–Mo(0) structure? Though it is clearly premature to venture any detailed explanation, we do note the following. (1) The introduction of RO ligands to the Mo_2^{4+} center weakens the M–M bonding, particularly the δ bond such that little, if any, M–M bonding is sacrificed in going from a Mo(II)–Mo(II) to the Mo(IV)–Mo(0) structure. (2) Metal–ligand bonding is optimized in the Mo(IV)–Mo(0) structure in that four hard alkoxide ligands coordinate to the Mo(IV) center and four soft phosphorus lone pairs coordinate to the Mo(0) center.

Further studies are in progress.[17]

Supplementary Material Available: Listings of atomic positional parameters together with a VERSORT drawing giving the atom number scheme and a complete listing of bond distances and angles (3 pages). See any current masthead page for ordering information.

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(8) Anal. Calcd (Found) for $Mo_2P_4C_{24}H_{60}O_4$: C, 39.6 (39.4); H, 8.3 (8.2); P, 17.0 (16.8); N, 0.00 (<0.03).

(9) $^{31}P\{^1H\}$ NMR δ 43.2 (rel H_3PO_4); ^1H NMR (21 °C toluene-d_8, 360 MHz) δ 4.22 (sept, $^3J_{HH}$ = 6 Hz, C*H*Me$_2$), 1.34 (d, $^3J_{HH}$ = 6 Hz, CH*Me*$_2$), 2.28, 0.30 (P*Me*$_2$), 2.79, 2.20, 1.27, 1.10 (PC*H*$_2$C*H*$_2$P).

(10) Crystal data for $Mo_2(O\text{-}i\text{-}Pr)_4(dmpe)_2$ at −155 °C: $a = 10.709$ (2) Å, $b = 18.902$ (5) Å, $c = 17.121$ (4) Å, $\beta = 92.05$ (1)°, $Z = 4$, $d_{calcd} = 1.397$ g cm^{-3}, and space group $C2/c$. Of the 2784 reflections collected (Mo Kα, $6° < 2\theta < 45°$), the 2006 having $F > 3\sigma(F)$ were used in the full least-squares refinement. All hydrogen atoms were located and refined isotropically; all non-hydrogen atoms were refined anisotropically. Final residuals were $R(F) = 0.027$ and $R_w(F) = 0.031$.

(11) Bennett, M. J.; Cotton, F. A.; Walton, R. A. *Proc. R. Soc. London, Ser. A* **1968**, *A303*, 175. *J. Am. Chem. Soc.* **1966**, *88*, 3866.

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(16) The Mo–O distance of 2.00 (1) Å (av) corresponds to a bond order of $1^1/_4$ and may be compared to an estimated single bond length of 2.06 Å and distances of 1.94 and 1.88 Å for Mo–OR bonds of order $1^1/_3$ and $1^2/_3$, respectively. See ref 6, 14, and: Chisholm, M. H.; Heppert, J. A.; Huffman, J. C. *Polyhedron* **1984**, *3*, 475.

(17) We thank the National Science Foundation and the Wrubel Computing Center for support and L.R.S. Van Der Sluys for obtaining ^{31}P NMR spectra.

Non-Koopmans' Effects in the Outer Valence Ionizations of Polyenes

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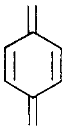
We wish to describe the results of our investigations of polyenes **1**–**4** by our transient photoelectron (TPE) method.[1,2] The data shed light on questions that have been raised[3] concerning the original experimental observations of the photoelectron spectra of **1**[1] and its 2,5-dimethyl derivative **3**[4] and the interpretational differences in the Koopmans' theorem[5] model (KTM)[6] and non-Koopmans' models (NMK).[6] The crucial factor that makes the present studies of **2** and **4** possible is the availability of sufficient quantities of (cyclophane) flash vacuum pyrolysis (FVP) precursors[7,8] since **1**–**4** are not kinetically stable.



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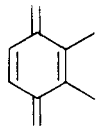

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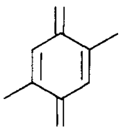

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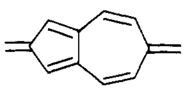

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Existing data from photoelectron spectroscopy (PES) overwhelmingly support the position[9] that the symmetry/energy sequence for the first several ionic states (IP_i) of molecules can be

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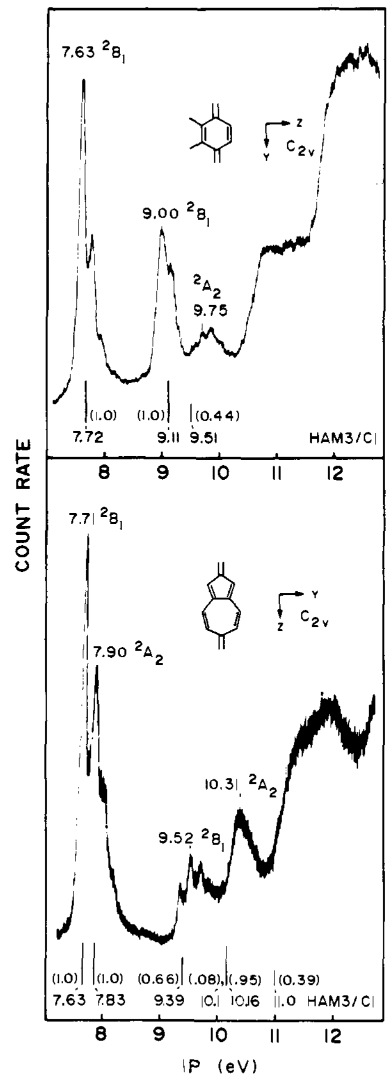

Figure 1. He(I) photoelectron spectra of 2,3-dimethyl-*p*-xylylene (top) and 2,6-azulylene (bottom). NKM results using a modified HAM3 (HAM3/CI) procedure are shown by the bars at the bottom of the spectra. Values in parentheses are calculated intensities.

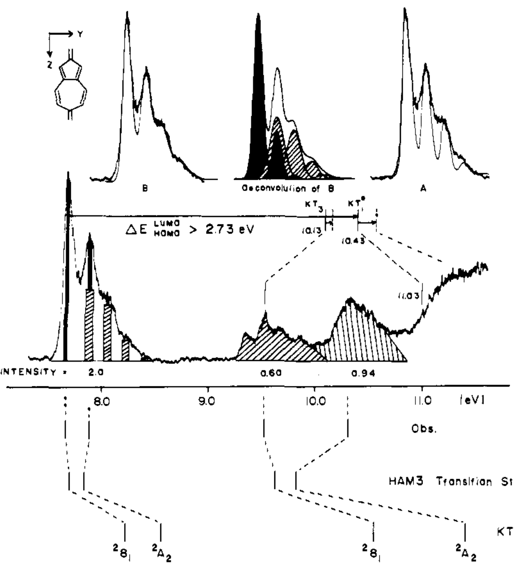

Figure 2. Outer valence PE spectrum of 2,6-azulylene. Inset A (top) is a Gaussian simulation of the 7.71-eV band using a single frequency (1550 cm^{-1}) and width (860 cm^{-1}). Inset B (top) is a Gaussian simulation of the 7.71-eV band using a two-state ($^2B_1$, $^2A_2$) model with two frequencies ($\nu_{2_{B_1}}$ = 1550, $\nu_{2_{A_2}}$ = 1450 cm^{-1}) and two widths ($\Delta_{1_{B_1}}$ = 860 cm^{-1}, $\Delta_{2_{A_2}}$ = 1433 cm^{-1}). Deconvolution of inset B shows $\nu_{2_{B_1}}$ as black and $\nu_{2_{A_2}}$ as crosshatched. The splitting diagram was derived from a simple 2 × 2 CI and the measured (0.6) relative area of the second $^2B_1$ band (9.5 eV). Results of the Koopmans' procedure (KTM) in CNDO/S and the HAM3 transition-state model are shown by the bars at the bottom.

assigned by the Koopmans' procedure (KTM, $IP_i \simeq -\epsilon_i$, the molecular orbital energy). Another view is to consider the orbitals as bases for configurations and to use linear combinations of antisymmeterized configurations (CI) as a means of describing electronic states.[6a-f] In our version of this procedure (NKM),[6] IP_i is the difference in energy of an ionic state including reorganization and correlation energy and the energy of the neutral ground state including CI stabilization. The most important observable difference in these models is the spectral intensity sharing that arises in the NKM between the Koopmans configurations (KT_a)[6] and non-Koopmans configuration (KT_i^*)[6]. Koopmans' approximation overlooks these additional NKM states and hence features in a PE spectrum that are their effect.

It has been suggested[3] that the weak (NKM) features we described in the original determination of the spectra of **1**[1] and its 2,5-dimethyl derivative[4] (**3**) were due to contaminating radical products. All of the results reported here were obtained with a sufficiently long flight path[2] (>10 cm) between furnace exit and photoionization to ensure that no reactive radical species would survive the time of flight.[2] Figure 1 (top) shows the TPE spectrum of **2** as obtained by FVP of its [2.2]paracyclophane[7] at 650 °C. The spectrum is hardly distinguishable from that previously observed for **2** under short flight path conditions. The important obvious feature is the significantly reduced relative area of the third band which qualitatively conforms to the NKM view. Figure 1 also contains the TPE spectrum of 2,6-azulylene (**4**), formed cleanly[8] by FVP of [2.2](2,6)azulenophane. The low relative intensity of the ~9.5-eV band is again suggestive of the NKM view.

Figure 2 contains an expansion of the outer valence ionization region of the PE spectrum of **4**. Close inspection of the first (~7.7 eV) band shape suggests that it corresponds to two ionic states. Inset B of Figure 2 is a calculated (Gaussian) composite band envelope composed of two progressions corresponding to two separate ionic states with different vibrational frequencies and line widths. Inset A contrasts a simulation which used a single progression and line width. The relative areas of the members of the two progressions in simulation B are matched by Franck–Condon calculated values ($2\delta_{(1^2B_1)}$ = 0.76, $2\delta_{(1^2A_2)}$ = 1.26) as indicated by the vertical bars under the observed first band envelope.

Figure 2 (bottom) contains the results of the CNDO/S[10] version of the KTM and those of the HAM3 transition-state method[11] for **4**. These calculations independently indicate near degeneracy the first two ionic states of **4**. We set the relative intensities of

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(12) The modifications used in the present case were linearly increased $f_{\mu\nu}$'s (1.00–1.05) and a modified repulsion algorithim which was charge dependent ($\gamma_{AB} = e^2/[R_{AB}{}^2(1 + Q(1 + q))^2 + (a_A + a_B)^2]^{1/2}$ where R_{AB} is the interatomic (A, B) distance, Q is a constant (0.185), q is the molecular charge, and $a_{A,B}$ are redetermined Ohno–Klopman constants (0.755 for carbon)). The values of the modified $f_{\mu\nu}$'s were chosen to fit the spectrum of **1** since recent[13] Green's function calculations strongly support the validity of the NKM interpretation of the position and intensity of a third π PE band in this case. The restricted CI space for the neutral ground state included pairwise double electron promotions and single excitations. The CI space for the ions was restricted to one-electron promotions from doubly occupied orbitals to the free electron orbital (f)[6] split pairwise promotions from the HOMO with one electron to f and one to an unoccupied orbital and split pairwise promotions from deeper doubly occupied orbitals with one electron to f and one to the LUMO. The HAM3/CI calculations for **4** were slightly complicated by the near degeneracy of the first two ionic configurations in that convergence does not give aufbau populations. The CI procedure used the molecular orbitals for the lowest of the two SCF configurations which was $^2B_1$ (lower than $^2A_2$ by 0.28 eV) and slightly modified orbital energies (0.110, 0.055 eV, HOMO, HOMO^{-1}).

(13) Von Niessen, W., private communication.

the 7.7-, 9.5-, and 10.3-eV bands as (2.0):0.6:0.94 as shown. Calculations on **4** with a modified version of HAM3 (HAM3/CI), which included the lowest 50 KT$_i$* configurations and in which the HOMO-LUMO gap ($\Delta E_{\mathrm{HOMO}}^{\mathrm{LUMO}}$) was varied, gave the results shown by the bars under the spectrum of **4** in Figure 1. The $\Delta E_{\mathrm{HOMO}}^{\mathrm{LUMO}}$ value obtained by this procedure (2.95 eV, lower limit) gives vertical bound electronic transitions for **4** at 371 ($^1B_2$), 325 ($^1A_1$) and 318 nm ($^1A_1$**). The latter values are in superficial agreement with observations[8] for neutral **4**. This procedure demonstrates one way a PE spectrum and the NKM view can be related to electronic properties of the corresponding neutral system.

In summary, the present results provide new experimental information that supports the view that shake-up phenomena[6a] are important in the low-lying ionic states of polyenes and may in some cases be comparable to through bond-through space effects.[14] We hope the present results will help to foster the wider view of the information implicit in photoelectron spectra of such systems.

Acknowledgment. This work was partially supported in part by the National Science Foundation. We are grateful to Dr. R. A. Wielesek for help in figure preparation.

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Cation-Stabilizing Auxiliaries: A New Concept in Biomimetic Polyene Cyclization

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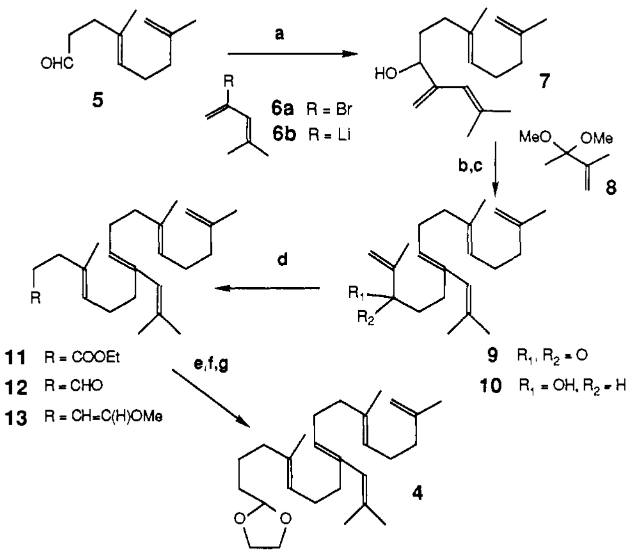
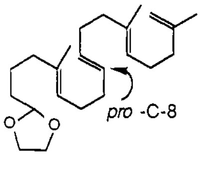
The one-step formation of two or three new rings by cyclization of polyenic substrates is now such a well-established art that very high yields can be achieved in favorable cases.[2] However, for more than 20 years serious effort has been directed toward a more ambitious and hitherto unattainable goal: the production of *four* new rings in one high-yielding, stereoselective step from acyclic polyenes. Such a reaction, involving the formation of six asymmetric centers at the bridgeheads, could seriously be compared to the biological conversion of squalene epoxide to protolanosterol. Most of the attempts in this direction have given incompletely cyclized products: for example, the nonenzymic cyclization of squalene epoxide affords tricyclic material with a five-membered C-ring as the only isolable polycycle.[3a] There have been only three partially successful experiments: tetracyclic products have been obtained with high *stereoselectivity*; yields, however, have been modest (2%,[3b] 30%,[4] and 34%[5]). Numerous attempts to improve upon these results, including the use of solid supports or ultrahigh pressures, have been abortive.[6] Consequently the feeling has emerged that the search for a *high-yielding* reaction may be a hopeless one without the help of the enzyme to overcome the unfavorable entropy of activation. Now we disclose a promising test case of a conceptually new approach to this problem: the modification of an internal double bond of the substrate by introduction of an auxiliary, so as to enhance the propagation of the cyclization process.

Scheme I[a]



[a] (a) 2.5 mol equiv of **6a**, 2.3 mol equiv of 1.6 M *n*-BuLi/hexanes, THF, -78 °C, 30 min, then 1 mol equiv of **5**; 75%. (b) 2 mol equiv of **8**, 0.4 mol equiv of 2,4-dinitrophenol, toluene, reflux, 17 h; 74%. (c) **9**, 1.5 mol equiv of 1 M DIBAL/hexanes, CH_2Cl_2, -78 °C, 30 min; 91%. (d) Excess triethylorthoacetate, catalytic propionic acid, reflux, 1 h; 90%. (e) 1.5 mol equiv of 1 M DIBAL/hexanes, ether, -90 °C, 15 min, then excess MeOH, -90 °C; 95% mass recovery, used without purification. (f) 3.5 mol equiv of methoxymethyltriphenylphosphonium chloride, 3.5 mol equiv of *s*-BuLi/cyclohexane, THF, -78 °C, 45 min, then 1 mol equiv of **12**, -78 - 20 °C; 51%. (g) **13**, excess ethylene glycol, 0.01 mol equiv of *p*-TsOH, DME, 21 °C, 17 h; 77%.

Formation of tetracyclic material from a substrate such as **1**[4] may be thought of as arising from two bicyclization reactions occurring in tandem. In this model, the first two rings would be expected to be formed in high yield;[2a] however, the resulting secondary cation **2** would not be sufficiently stabilized for efficient initiation of a second bicyclization.[7] Modification of cation **2** to a type known to be a good initiator was therefore envisaged. Introduction of a cation-stabilizing auxiliary (for example, an isobutenyl group) at *pro*-C-8 in polyene **1** would lead, after formation of the first two rings, to a tetrasubstituted allylic cation **3** which would be predicted to be an effective initiator for further cyclization[8] (the stereochemical consequence was not assured, however; see below). In the absence of conclusive mechanistic information on tetracyclizations this rationale was necessarily speculative, although the detection of bicyclic material resulting from elimination of a proton from a cation related to **3** in a similar



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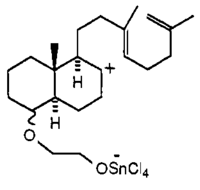

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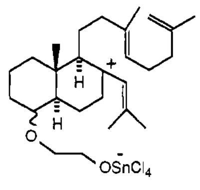

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(1) The X-ray analyses reported herein were performed by Professor Schubert, Institut für Anorganische Chemie der Universität Würzburg.

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(7) The activation energy for reaction of the destabilized cationic site of **2** with the adjacent double bond is probably low relative to that for conformational reorganization of the remaining polyene chain. Significant participation by the terminal olefinic bond is therefore unlikely to occur. For an undesirable result from a polyene cyclization initiated by an inadequately stabilized cation, see: Peters, J. A. M.; Posthumus, T. A. P.; van Vliet, N. P.; Zeelen, F. J.; Johnson, W. S. *J. Org. Chem.* **1980**, *45*, 2208-2214.

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