ions are m/z 60 and 62, respectively. Thus, pathway A must be the only one operative. *We can therefore state unequivocally that those $C_3H_6O^{+\cdot}$ ions from 1,4-dioxane which show a $C_2H_4^{+\cdot}$ transfer must have the acyclic structure* **1**[7,8] *and have a lifetime of at least 1 ms.* Our results thus provide experimental substantiation of the ab initio prediction[1] of a stable C···C ring-opened isomer of the trimethylene oxide cation radical.

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(7) The possibility that ion **1** could undergo a 1,2-hydrogen shift to give another low-energy species $CH_3CHO^{+\cdot}CH_2$,[1] which could then be the ion which transfers $C_2H_4^{+\cdot}$, can be ruled out. The above $C_3H_6O^{+\cdot}$ isomer, generated from fragmentation of the molecular ions of either 4-methyl-1,3-dioxolane[1] or 4,5-dimethyl-1,3-dioxolane, shows reactions with both acetonitrile and pyridine[9] which are different from those of the $C_3H_6O^{+\cdot}$ ion from 1,4-dioxane.

(8) We consider that the transfer of $C_2H_4^{+\cdot}$ from the molecular ion of trimethylene oxide to acetonitrile is also likely to occur via the C···C ring-opened ion **1**.

(9) Baumann, B. C.; MacLeod, J. K., unpublished results.

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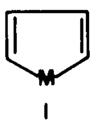
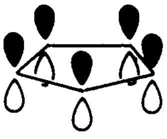
Cyclic 4π Stabilization. Combined Möbius–Hückel Aromaticity in Doubly Lithium Bridged $R_4C_4Li_2$ Systems[1]

Sir:

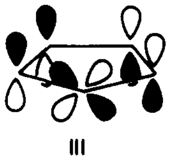
How can cyclic 4π electron topologies, usually associated with "antiaromaticity", be stablized? We propose a simple solution to this problem: two energetically favorable molecular orbitals, one Hückel and one Möbius in character,[2] are utilized. Consider the generalized metallocycle, I, in which M contributes no π electrons but offers vacant orbitals of p (II) and d (III) symmetry. The four π electrons of the butadiene moiety can now be delocalized effectively in two MO's, II (Hückel type, no phase inversions) and III (Möbius type, one phase inversion; the nodal plane passing through M does not count).[2] Since different basis sets of atomic orbitals are utilized in II and III, combined Hückel–Möbius character results.



I



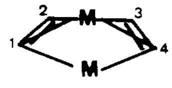
II



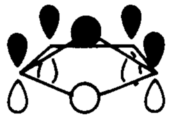
III

Although many metallacycles are known[3,4] and the possibility of d-orbital involvement (III) has been considered in detail,[3,5] we are not aware of any 4π systems (I) which demonstrate the special stabilization associated with "aromaticity".[6] Perhaps the C–M σ bonds in I are too long to permit effective overlap in orbitals like III. There is a way around this diffculty.

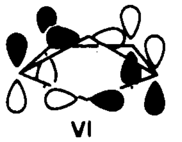
Instead of completing the ring by means of a coplanar atom (M in I), this can be achieved by two atoms or groups, M in IV, placed roughly between C_1 and C_4 but above and below the carbon plane. This would confer greater geometrical flexibility with regard to the C_1–C_4 separation. In Hückel MO V, s orbitals of M are utilized; in Möbius MO VI, the involvement of M p orbitals is required.



IV(C_{2v})

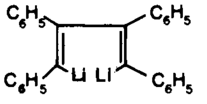


V

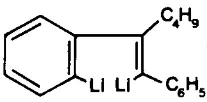


VI

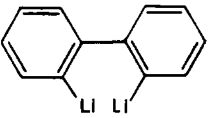
We think it is likely that systems like IV are already known experimentally, although their nature has not been recognized. Diphenylacetylene dimerizes with metallic lithium to give a dilithiated species,[7] traditionally written in the all-cis form, VII, perhaps because of its utility in preparing various heterocycles (I).[4] Diphenylacetylene reacts with n-butyllithium anomalously. The reaction does not stop with a simple triple bond addition; specific metalation of a single "pseudoacidic" ortho phenyl hydrogen occurs as well to give VIII.[8] VII, VIII, and o,o'-dilithiobiphenyl (IX)[4c] can be regarded as derivatives of IV-Li possibly favoring double lithium bridging.



VII



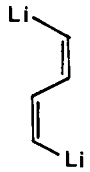
VIII



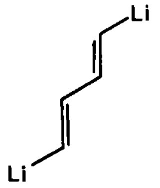
IX

We have investigated this problem by means of molecular orbital calculations. Numerous trial structures for $C_4H_4Li_2$ were examined by utilizing the semiempirical MNDO method.[9] The most energetically competitive structures (including IV and X–XIII) were recalculated, by use of the minimal STO-3G basis set and full-geometry optimization within the symmetries selected.[10] Single point split valence basis 4-31G//STO-3G calculations followed; the lowest energy structural forms (IV-Li and XIII-Li) were then optimized with the 4-31G basis (4-31G//4-31G).[10] Table I summarizes the energies and provides some geometrical information; the supplementary material can be consulted for the full geometries.

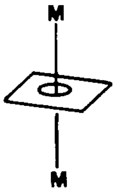
X(C_{2v})



XI(C_{2h})



XII(C_{2h})



XIII(D_{4h})

In addition to the structures shown (IV and X–XIII), lower symmetry alternatives were also considered. These include C_s and

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(1) Presented at the Annual Chemical Congress, The Chemical Society, Durham, England, April 1980 (See: *Chem. Brit.* **1980**, *16*, 385) and at the Royal Society of Chemistry International Symposium, "Metall-Organics in Organic Synthesis", Swansea, Wales, July 1980.

(2) Heilbronner, E. *Tetrahedron Lett.* **1964**, 1923. Zimmerman, H. *Acc. Chem. Res.* **1971**, *4*, 272.

(3) For leading references see: Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.

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(6) Bushby, R. J.; Patterson, A. S. *J. Organomet. Chem.* **1977**, *132*, 163. Bushby et al. have called attention to the 4π Möbius character of the bridged structure of allyllithium. Also see: Reetz, M. T. *Tetrahedron* **1973**, *29*, 2189.

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(9) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.*, **1977**, *99*, 4899, 4907. The parameterization for lithium (Thiel, W.; Clark, T., unpublished) is still in the development stage.

(10) The Gaussian 76 program with the standard basis sets was used: Binkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. *QCPE* **1979**, *11*, 368.

Table I. Energies and Geometries of $C_4H_4Li_2$ Isomers

	total energies, hartrees		relative energies, kcal/mol		bond lengths, Å (STO-3G)[a]				
structure	STO-3G//STO-3G	4-31G//STO-3G	STO-3G//STO-3G	4-31G//STO-3G	$r(C_1-C_4)$	$r(C_1-C_2)$	$r(C_2-C_3)$	$r(C_1-M)$	$r(C_2-M)$
IV-Li	-166.58116	-168.40602	0.0	0.0	2.966	1.369	1.517	1.968	2.188
		-168.41671[b]		(0.0)[b]	2.505[b]	1.336[b]	1.502[b]	2.074[b]	2.413[b]
X	-166.42868	-168.32652	95.7	49.9	3.324	1.333	1.498	1.908	3.008
XI	-166.46491	-168.35050	73.0	34.8	3.758	1.329	1.494	1.863	2.412
XII	-166.47343	-168.33613	67.6	43.9	3.805	1.342	1.494	1.776	2.026
XIII-Li	-166.57482[c]	-168.36612	4.0	25.0	1.478	1.478	1.478	1.952	1.952
		-168.37482[b]		(26.3)[b]	1.473[b]	1.473[b]	1.473[b]	2.069[b]	2.069[b]

[a] The usual butadiene numbering was used. [b] 4-31G//4-31G. [c] Reference 12.

C_2 distortions of IV (in which the atoms were shifted out of the σ_v symmetry plane) and relatives of XI and XII twisted around the C–C single bond. The energies did not improve.

A number of additional structural possibilities were probed, but these were not competitive in energy with the global minimum, IV-Li. In particular, a structure in which a five-membered ring, comprised of four carbons and a lithium atom, was capped by lithium (as in the ferroles)[11] proved not to be an energy minimum.

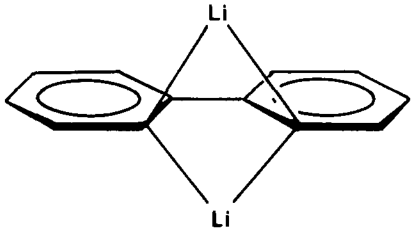
Our combined Möbius–Hückel aromatic candidate (IV-Li) is indicated to be remarkably stable relative to all other forms examined, especially X, suggested by the traditional cis-planar representations of VII–IX.[4] X is unfavorable, both sterically and electronically. XI, the *s*-trans rotamer of X, and the all-trans isomer, XII, are more favorable energetically, but neither can compete with IV-Li. The energy gained on cyclization, XI → IV-Li, 35 kcal/mol (4-31G//STO-3G), provides a good estimate of the resonance energy of our newly proposed Hückel-Möbius aromatic system, IV-Li.

Alternating C–C bond lengths are indicated in the structure of IV-Li, whereas more nearly equal bond lengths are generally associated with Hückel aromatics. The different C_1–C_2 (1.37 Å) and C_2–C_3 (1.52 Å) distances are a natural consequence of the occupation of the two non-degenerate orbitals, V and VI. Despite the short Li···Li distance in IV-Li (2.4 Å), the overlap population indicates an antibonding interaction.

IV-Li also competes successfully energetically against the Hückel aromatic alternative, XIII-Li.[12] XIII can be considered to be a derivative of the 6π cyclobutadiene dianion, $C_4H_4^{2-}$,[13] interacting on top and bottom faces with two M^+ cations. Alternatively, XIII-Li can be regarded as one of the simplest "inverse sandwiches"[14] obeying a six interstitial electron rule[15] in which three stablized orbitals are utilized to bind a four-membered ring (C_4H_4 in XIII) and two caps (M in XIII) together.[12] This rule also applies to the BeH capped analogue (XIII-BeH) and to its isoelectronic relatives, the carborane, $C_2B_4H_6$, and the borane, $B_6H_6^{2-}$.[12]

Despite its favorable electronic structure, XIII-Li is indicated (4-31G//4-31G) to be 26 kcal/mol less stable than IV-Li. Both IV and XIII represent energy minima on the $C_4H_4Li_2$ potential-energy surface; their interconversion is orbital symmetry forbidden. In this context, the analysis by Thorn and Hoffmann[11] of transition-metal complexes closely related in geometry to IV and XIII is quite illuminating. However, the ligands examined were not isolobal with Li.

Isolobal transition-metal analogues may be realizable if IV exhibits "aromaticity". It is also possible that crystalline derivatives of IV, e.g., VII–IX, amenable to X-ray analysis, might be prepared.[4b] The symmetrical double bridging exemplified by IV-Li, which may be present in VII–IX as well (e.g., XIV),[16] is



XIV(C_{2v})

a general feature of polylithium compounds, at least as is indicated by our published[17] and unpublished[1] calculations on numerous systems.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie. We thank Dr. E. D. Jemmis for calculations on XIII,[12] Professor W. Heilbronner for perceptive comments, Dr. J. Chandrasekhar for much help, the Regionales Rechenzentrum for assistance, and Professor R. Hoffmann for his interest.

Supplementary Material Available: STO-3G//STO-3G and 4-31G//4-31G geometries (coordinates and Z matrices) for IV–Li and X–XIII (5 pages). Ordering information is given on any current masthead page.

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(11) Thorn, D. L.; Hoffmann, R. *Inorg. Chem. 1978, 17*, 126.

(12) Jemmis, E. D. Ph.D. thesis, Princeton University, 1978. Jemmis, E. D.; Schleyer, P. v. R., to be published. The possibility of a benzocyclobutadienyl dianion structure for VIII was specifically considered in ref 8b, but ruled out. A metallacycle-ion-pair alternative was suggested.

(13) Garratt, P. J.; Zahler, R. *J. Am. Chem. Soc.* **1978**, *100*, 7753 and refs cited therein.

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(16) MNDO calculations indicate the doubly bridged form of 0,0'-dilithiobiphenyl (XIV) to be 59 kcal/mol more stable than planar (C_{2v}) IX and 22 kcal/mol more stable than a C_2 conformation fixed at a 90° angle.

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Thionium Ions as Carbonyl Substitutes. Synthesis of Cyclic Imino Thioethers and Lactams

Sir:

The unparalleled role of the carbonyl group in organic synthesis suggested consideration of functional equivalents. Foremost among the possibilities stands the thionium ion whose higher polarity and low π bond strength led us to refer to it as "super carbonyl".[1] Its

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(1) Trost, B. M.; Reiffen, M.; Crimmin, M. T. *J. Am. Chem. Soc.* **1979**, *101*, 257 and references therein. Reetz, M. T.; Huttenhain, S.; Walz, P.; Lowe, U. *Tetrahedron Lett.* **1979**, 4971. Brinkmeyer, R. S. *Ibid.* **1979**, 207. Mizyuk, V. L.; Semenovsky, A. V. *Ibid.* **1978**, 3603. Kozikowski, A. P.; Ames, A. *J. Am. Chem. Soc.* **1980**, *102*, 860.

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