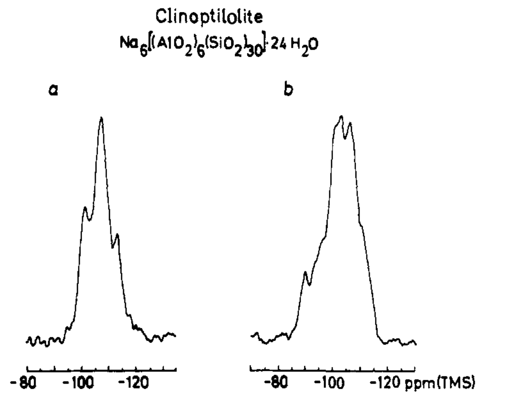

Figure 7. ^{29}Si NMr spectra of clinoptilolite: (a) without and (b) with cross-polarization. Polarization transfer from the ^1H nuclei in hydroxyl groups leads to significant enhancement of the $Si(OH)_2$ and SiOH lines.

of Ca^{2+} ions as was the case in chabazite.

Clinoptilolite. The crystal structure of clinoptilolite $T_{10}Q_{20}$ Dzegvi, GA, Si/Al = 5) has not been unequivocally determined to our knowledge, although similarity with the structure of heulandite has been proposed.[7] Investigation of model structures with $T_{10}Q_{20}$ as the main unit predict the highest concentration for Si(1Al) units in spite of the high Si/Al ratio. The ^{29}Si chemical shift of the most intense line (−106.9 ppm) in the clinoptilolite spectrum lies in the shift range of Si(0Al) units. It is therefore possible that the structure of clinoptilolite is not based on the $T_{10}O_{20}$ units. The intensity in the region of the signal at −100 ppm is substantially increased in CP experiments and a shoulder appears at about −90 ppm (Figure 7). In these ranges lie the ^{29}Si NMR signals of SiOH and $Si(OH)_2$ groups.[9]

Concluding Remarks

The overall results of the ^{29}Si NMR study of the structure of zeolites lead to the following conclusions.

(1) ^{29}Si NMR spectra provide qualitative and semiquantitative information about the zeolite structure and especially about Si/Al ordering in the aluminosilicate framework. The ^{29}Si chemical shifts display a regular dependence upon the number of AlO_4 tetrahedra connected to the SiO_4 tetrahedron under study.

(2) The regularities in ^{29}Si chemical shifts were used to establish the presence in zeolites of silicon tetrahedra of various degree on aluminum substitution and the type and regularity of distribution of the Si and Al atoms in the lattice.

(3) Independent information about the Si/Al ordering can be used to supplement X-ray structure studies of zeolites. Possible examples of anti-Loewenstein AlOAl bridging were found in synthetic and natural zeolites.

(4) Cross-polarization techniques can be used to establish the presence of SiOH and $Si(OH)_2$ groups in the samples studied.

(5) All the NMR methods used in this study are applicable to the investigation of microcrystalline or amorphous powder samples as well. The line widths correlate with the long-range regularity of the lattice.

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1,2-Dilithioethane. A Molecular Orbital Study

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Abstract: The potential energy surface of $LiCH_2CH_2Li$ was examined at several levels of ab initio theory, e.g., 3-21G (geometries) and MP2/6-31G*//3-21G (energies). The global energy minimum was found to be **1**, C_{2h}, with a trans conformation (dihedral angle, ϕ_{LiCCLi} = 180°) but an unusual partially bridged geometry (∠LiCC = 73.2°). However, the symmetrically trans doubly bridged structure (**2**, D_{2h}), a transition state for dyotropic rearrangement, is only 1.9 kcal/mol higher in energy. The rotational potential energy surface is characterized by a gauche minimum (**3**, C_2, ∠LiCC = 66.4°) at ϕ_{LiCCLi} = 84.0°, 8.0 kcal/mol less stable than **1**. Only a small rotational barrier separates **3** and **1** when the dihedral angle is increased from 84° to 180°, but the ϕ_{LiCCLi} = 0° barrier (corresponding to the eclipsed structure, **4**) is much higher in energy, 28.9 kcal/mol above **1**. A cis dyotropic transition state, **3′** (C_{2v}), is 2.4 kcal/mol less stable than **3** and 10.4 kcal/mol less stable than **1**. Although **1** is indicated to be marginally unstable thermodynamically toward dissociation into ethylene and Li_2, the lithium substituents interact in a mutually stabilizing manner. The similarities of $C_2H_4Li_2$ geometries **1** and **2** with known X-ray structures of more highly substituted 1,2-dilithium compounds and with the geometries of ethane derivatives substituted vicinally by other metals are emphasized. For comparison, C_2H_6 in doubly bridged (**7**, D_{2h}) diborane-like and in quadruply bridged (**8**, D_{4h}) geometries were examined. These are very unstable, lying 149 and 437 kcal/mol (MP2/6-31G*//6-31G*), respectively, above D_{3d} ethane (**5**).

Although 1,2-dilithioethane has been claimed only as a poorly characterized pyrophoric gray powder,[2a] and as a possible reaction intermediate,[2b] this species is inherently interesting as the simplest possible ethane vicinally substituted by two metals. 1,2-Dilithioethane also serves as a model for several dilithio derivatives for which X-ray structures are available: 9,9′-bifluorenyl–bis(lithium tetramethylethylenediamine),[3] stilbene–bis(lithium tetramethylethylenediamine),[4] and acenaphthylene–bis(lithium

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(1) Dissertation, Technische Hochschule Darmstadt, 1977.
(2) (a) H. Kuus, *Uch. Zap. Tartu Gos. Univ.*, 133 (1966); *Chem. Abstr.*, **69**, 67443 (1968); *Uch. Zap. Tartu Gos. Univ.*, 245 (1968); *Chem. Abstr.*, **71**, 49155 (1969); (b) V. Rautenstrauch, *Angew. Chem., Int. Ed. Engl.*, **14**, 259 (1975).
(3) M. Walczak and G. D. Stucky, *J. Organomet. Chem.*, **98**, 313 (1975).

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Table I. Total Energies of 1,2-Dilithioethanes **1–4**

	total energies, hartrees						
geometry	STO-3G// STO-3G	3-21G//3-21G	4-31G//4-31G	MP2/4-31G// 4-31G	6-31G*//3-21G	6-31G*//4-31G	MP2/6-31G*// 3-21G
1, C_{2h}	−91.72792	−92.35017	−91.75651[a]	−92.96500	−92.86951	−92.86905	−93.16718
5, D_{2h}	−91.72245	−92.34658[b]	−92.75436[c]	−92.96277[d]	−92.86265	−92.86299	−93.16410
3, C_2		−92.33741[e]	−92.74259		−92.85819		−93.15437
3′, C_{2v}	−91.68751	−92.33617	−92.74173[f]	−92.95040[g]	−92.88502	−92.85527	−93.15059
4, C_{2v}	−91.66665	−92.30347	−92.71341	−92.91621	−92.82570	−92.82609	−93.12117

[a] Triplet **1** is not an energy minimum; optimization leads to triplet 2. [b] Triplet: −92.35835 au. [c] Triplet: −92.76163 au. [d] Triplet: −92.93488 au. [e] Triplet dissociates upon optimization into Li_2 and C_2H_4. [f] Triplet: −92.76831 au. [g] Triplet: −92.93799 au.

Table II. Relative Energies of 1,2-Dilithioethanes **1–4**

	relative energies, kcal/mol						
geometry	STO-3G// STO-3G	3-21G//3-21G	4-31G//4-31G	MP2/4-31G// 4-31G	6-31G*// 3-21G	6-31G*// 4-31G	MP2/6-31G*// 3-21G
1, C_{2h}	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2, D_{2h}	3.4	2.3	1.3	1.4	4.3	3.8	1.9
3, C_2		8.0	8.7		7.1		8.0
3′, C_{2v}	25.4	8.8	9.2	9.2	9.1	8.7	10.4
4, C_{2v}	38.5	29.3	27.0	24.3	27.5	27.0	28.9

Table III. Optimized Geometries of Dilithioethanes[a]

molecule	basis set	C–C	C–Li	C–H	Li–Li	H–H	∠CCLi	∠HCH	∠CCΘ[b]	∠LiΘLi[c]
1, C_{2h}	STO-3G	1.544	1.856	1.092	3.559	1.818	72.2	112.6	139.9	
	3-21G	1.593	1.955	1.092	3.772	1.817	73.2	112.6	139.2	
	4-31G	1.565	1.941	1.088	3.745	1.818	73.3	113.2	144.3	
2, D_{2h}	STO-3G	1.536	1.921	1.082	3.520	1.864	66.4	119.1		
	3-21G	1.548	2.028	1.080	3.749	1.859	67.6	118.7		
	4-31G	1.535	2.011	1.080	3.717	1.850	67.6	117.9		
3, C_2	3-21G	1.610	2.004	1.088[d]	2.458	1.726	66.4	115.1[f]	109.8[h]	84.0[k]
				1.104[e]				184.7[g]	−58.5[i]	
	4-31G	1.587	1.989	1.087[d]	2.454	1.723	66.9	116.2[f]	111.1[h]	82.2[k]
				1.100[e]				182.5[g]	−59.0[i]	
3′, C_{2v}	STO-3G	1.524	1.966	1.089	2.208	1.723	67.2	104.6	124.4	75.0
	3-21G	1.624	1.998	1.092	2.392	1.726	66.0	104.4	127.9	81.8
	4-31G	1.599	1.986	1.090	2.392	1.724	66.3	104.5	130.3	82.3
4, C_{2v}	STO-3G	1.568	2.040	1.086	3.675	1.718	121.1	104.4	119.3	
	3-21G	1.601	2.035	1.097	3.838	1.732	123.3	104.2	120.7	
	4-31G	1.571	2.032	1.096	3.841	1.733	124.0	104.5	122.9	

[a] Bond lengths in Å, angles in degrees. [b] Θ = bisector of HCH. [c] Θ designates a point in the center of the CC bond. [d] C_1–H_1. [e] C_1–H_2. [f] ∠$C_2C_1H_1$. [g] ϕ $LiC_2C_1H_1$. [h] ∠$C_2C_1H_2$. [j] ϕ $LiC_2C_1H_2$. [k] ϕ LiCCLi.

tetramethylethylenediamine).[5] In all three of these structures, the lithium atoms adopt trans doubly bridged arrangements akin to **2**. Partially bridged trans structures, like **1**, have been found in stilbene-bis(lithium pentamethyldiethylenetriamine (PMDTA))[4] and in several zirconium derivatives,[6] as will be discussed below.

Doubly bridged structures have been considered theoretically by Hoffmann and Williams[7] and particularly by Reetz,[8] who coined the name "dyotropic rearrangement" for processes whereby two vicinal groups exchange places on a carbon framework. Such rearrangements, in principle, could proceed via **2** or via the cis doubly bridged equivalent, **3′**. We have already examined such double bridging in C_2Li_2[9] and in *cis*- and *trans*-LiCH=CHLi.[10]

(4) M. Walczak and G. D. Stucky, *J. Am. Chem. Soc.*, **98**, 5531 (1976).
(5) W. E. Rhine, J. H. Davis, and G. D. Stucky, *J. Organomet. Chem.*, **134**, 139 (1977).
(6) W. Kaminsky, J. Kopf, H. Sinn, and H.-J. Vollmer, *Angew. Chem.*, **88**, 688 (1976); *Angew. Chem., Int. Ed. Engl.*, **15**, 629 (1976). Also see: K. I. Gell, G. M. Williams, and J. Schwartz, *J. Chem. Soc., Chem. Commun.*, 550 (1980).
(7) R. Hoffmann and J. E. Williams, Jr., *Helv. Chim. Acta*, **55**, 67 (1972).
(8) M. T. Reetz, *Angew Chem.*, **84**, 161, 163 (1972); *Tetrahedron*, **29**, 2189 (1973); *Adv. Organomet. Chem.*, **16**, 33 (1977).
(9) Y. Apeloig, P. v. R. Schleyer, J. S. Binkley, J. A. Pople, and W. C. Jorgensen, *Tetrahedron Lett.*, 3923 (1976).
(10) Y. Apeloig, T. Clark, A. J. Kos, E. D. Jemmis, and P. v. R. Schleyer, *Isr. J. Chem.*, **20**, 43 (1980). This paper lists references to earlier calculations on organic polylithium compounds.

The only prior ab initio examination of $LiCH_2CH_2Li$[11] was concerned with the rotational potential surface using standard geometries (rigid rotation, see Figure 1). As expected on the basis of strong dipolar repulsions, the trans conformation was the most stable; interestingly, no gauche minimum was indicated, only a flattening of the potential function around a torsional angle of ca. 100°. We report here a much more extensive examination of the $C_2H_4Li_2$ energy surface with full geometry optimization. For comparison, C_2H_6 has also been calculated in doubly bridged (D_{2h}) and quadruply bridged (D_{4h}) geometries.

Computational Methods

Calculations were carried out at the restricted Hartree–Fock (RHF) level using the Gaussian programs[12] with the standard basis sets. The structures were completely optimized within each assumed symmetry using a routine which combines the Davidon–Fletcher–Powell[13] multiparameter search with analytically evaluated atomic forces.[14] Single point calculations using the

(11) L. Radom, P. J. Stiles, and M. A. Vincent, *J. Mol. Struct.*, **48**, 431 (1978).
(12) J. S. Binkley, R. A. Whiteside, P. C. Hariharan, R. Seeger, J. A. Pople, J. A. Hehre, and M. D. Newton, *QCPE*, **11**, 368 (1979); J. A. Pople et al., *ibid.*, **13**, 406 (1981).
(13) R. Fletcher and M. D. Powell, *Comput. J.*, **6**, 163 (1963); W. C. Davidon, *ibid.*, **10**, 406 (1968); D. Poppinger, *Chem. Phys. Lett.*, **34**, 1975 (1975).

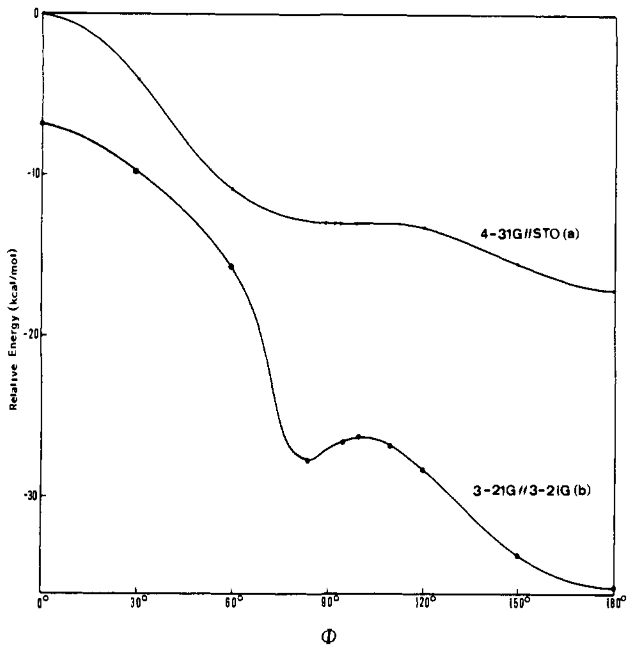


Figure 1. Rotational potential surface of 1,1-dilithioethane: (a) rigid rotation with standard geometries, 4-31G//STD; (b) optimized geometries, 3-21G//3-21G. The energy difference at ϕ = 0° reflects the energy gain on optimization (see text).

Table IV. Total Energies (Hartrees) and Relative Energies (kcal/mol) for Conformations of 1,2-Dilithioethane

rotation optimization (3-21G//3-21G)			rigid rotation (4-31G//STD)		
ϕ^a	total energy	rel energy	ϕ^a	total energy	rel energy
0°	−92.30347	0.0	0°	−92.70326^b	0.0^c
30°	−92.30894	−0.9	30°	−92.71016	−4.3
60°	−92.31835	−8.6	60°	−92.72047^b	−10.8
84°	−92.33741	−21.3	90°	−92.72388	−12.9
95°	−92.33555	−20.1	92°		−13.1^d
100°	−92.33504	−19.8	94°	−92.72394^b	−13.0
110°	−92.33611	−20.5	109°	−92.72408^b	−13.1
120°	−92.33846	−22.0	120°	−92.72450^b	−13.3
150°	−92.34658	−27.0	150°	−92.73288	−15.4
180°	−92.35017	−29.3	180°	−92.73034^b	−17.0^c

^{a} Torsional angle, LiCCLi. ^{b} Reference 11. ^{c} Energy lowerings due to geometry optimization (4-31G//4-31G) are 6.4 and 16.4 kcal/mol at ϕ = 0° and 180°, respectively. ^{d} Calculated from the first derivative of the torsional potential function $V(\phi)$.

4-31G[15a] (5-21G[15b] for lithium is implied) and 3-21G[15c] optimized structures employed the polarized (i.e., with d-type functions on Li and C) 6-31G* basis set.[15d] These are designated, e.g., 6-31G*//4-31G. The corrections due to electron correlation were estimated at the 6-31G* level using second-order Møller–Plesset theory (MP2/6-31G*//3-21G).[16] The energies of the triplet states were investigated using MNDO[17] and UHF ab initio theory.[12] For C_2H_6, the 6-31G** basis set, with additional p-type functions on H,[15d] was also employed.

(14) The analytic force evaluation routines (H. B. Schlegel, S. Wolfe, and F. Bernardi, *J. Chem. Phys.*, **63**, 3632 (1975)) were incorporated by Dr. Schlegel and by Dr. J. Chandrasekhar in the programs in use at Erlangen.

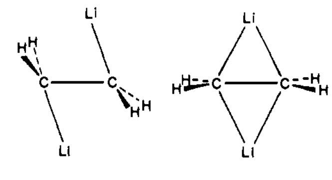
(15) (a) W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, **56**, 4233 (1972); (b) J. D. Dill, and J. A. Pople, *ibid.*, **62**, 2921 (1975); (c) J. S. Binkley, J. A. Pople, and W. J. Hehre, *J. Am. Chem. Soc.*, **102**, 939 (1980); (d) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973).

(16) J. S. Binkley and J. A. Pople, *Int. J. Quantum Chem. Symp.*, **9**, 229 (1975).

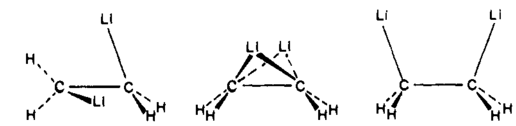
(17) MNDO: M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899, 4907 (1977); M. J. S. Dewar and H. S. Rzepa, *ibid.*, **100**, 58, 777 (1978); M. J. S. Dewar and M. L. McKee, *ibid.*, **99**, 5231 (1977); M. J. S. Dewar, M. L. McKee, and H. S. Rzepa, *ibid.*, **100**, 3607 (1978). Lithium parameterization by W. Thiel and T. Clark (unpublished) is provisional. See footnote 29.

Results and Discussion

The total and relative energies and the geometries for 1,2-dilithioethane structures **1**, **2**, **3**, **3′**, and the eclipsed form, **4**, are given in Tables I–III. The global energy minimum (**1**, C_{2h}) has a trans conformation, but with an unusual partly bridged geometry (∠LiCC = 73.3°, 4-31G). This recalls the partially bridged form of *trans*-1,2-dilithioethylene, with ∠LiCC = 87.0° (4-31G).[10] The energy gained by partial bridging in **1**, 16.4 kcal/mol (4-31G), can be assessed by comparing the standard geometry (180° dihedral angle) $LiCH_2CH_2Li$ energy of Radom et al.[11] with that of fully optimized **1**. The symmetrically trans doubly bridged structure **2**, (D_{2h}), the transition state for dyotropic rearrangement, is 1.9 kcal/mol higher in energy than **1** (MP2/6-31G*//3-21G). (The energy difference between partially bridged *trans*-1,2-dilithioethylene and the symmetrically bridged (D_{2h}) form was much higher, e.g., 54.4 kcal/mol at 6-31G*//4-31G.[10]) Although the energy favoring **1** over **2** is small, **1** is indicated to be more stable at all levels of theory examined (Table II). This small energy



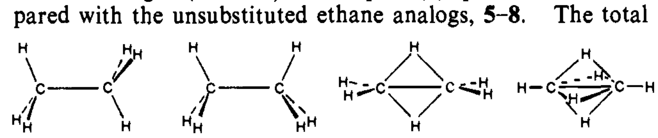
1,C_{2h} **2**,D_{2h}



3,C_2 **3′**,C_{2v} **4**,C_{2v}

difference between **1** and **2** is reflected in the different X-ray structures mentioned above. Stilbene–bis(lithium pentamethyldiethylenetriamine) has a partly bridged geometry, but the use of a different complexing ligand, tetramethylenediamine (TMEDA), results in a symmetrical bridged structure, similar to **2**.[4] Small energy changes due to crystal packing forces or differences in solvation evidently are sufficient to tilt the balance in favor of either structural type, **1** or **2**. The cis doubly bridged form (**3′**, C_{2v}), 8.7 kcal/mol above **1**, is somewhat less stable. Eclipsed **4**, which can be taken to model the geometry expected in certain constrained bicyclic vicinal dilithium systems,[18] is much higher in energy, 27.0 kcal/mol above **1**. Rotational potential data are given in Table IV.

These bridged (**2** and **3′**) and eclipsed (**4**) species can be compared with the unsubstituted ethane analogs, **5**–**8**. The total



5,D_{3d} **6**,D_{3h} **7**,D_{2h} **8**,D_{4h}

energies and geometries for staggered (**5**), eclipsed (**6**), doubly bridged (**7**), and quadruply bridged (**8**) ethane are given in Tables V and VI. At the MP2/6-31G*//6-31G* level, the energy barrier for the trans dyotropic rearrangement of ethane (via **7**, a diborane-like doubly bridged structure)[7,8] is 149 kcal/mol. While this value is considerably less than an earlier ab initio estimate,[19] the experimental C–H bond dissociation energy in ethane is 98 kcal/mol.[20] Hence, structures like **7** and **8** have no chance of

(18) R. N. McDonald and C. A. Curi, *J. Am. Chem. Soc.*, **99**, 7078 (1977).

(19) R. J. Buenker, S. D. Peyerimhoff, L. C. Allen, and J. L. Whitten, *J. Chem. Phys.*, **45**, 2835 (1966).

(20) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley-Interscience, New York, 1976.

Table V. Total and Relative Energies of C_2H_6 Structures **5–8**

	total energies, hartrees					relative energies, kcal/mol				
geometry	STO-3G// STO-3G	4-31G// 4-31G	6-31G*// 6-31G*	6-31G**// 6-31G*	MP2/6-31G*// 6-31G*	STO-3G// STO-3G	4-31G// 4-31G	6-31G*// 6-31G*	6-31G**// 6-31G*	MP2/6-31G*// 6-31G*
5, D_{3d}	−78.30618[a]	−79.11593[a]	−79.22876	−79.23823	−79.49451	0.0	0.0	0.0	0.0	0.0
6, D_{3h}	−78.30160[a]	−78.11151[b]	−79.22240	−79.23321	−79.48937	2.87	2.77	3.99	3.15	3.23
7, D_{2h}	−77.96889	−78.85466	−78.97031	−78.98786	−79.25715	211.7	163.9	162.2	157.1	148.9
8, D_{4h}	−77.30344	−78.32567	−78.45215	−78.49100	−78.79739	629.2	495.9	487.3	468.9	437.4

[a] W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, 93, 808 (1971). [b] J. P. Colpa, H. B. Schlegel, and S. Wolfe, *Can. J. Chem.*, 54, 526 (1976).

Table VI. Optimized Geometries[a] of C_2H_6 Isomers **5–8**

molecule	basis set	C–C	C–H[b]	∠HCH[b]	C–H[c]	∠CHH[c]
5, D_{3d}	STO-3G[d]	1.538	1.086	108.2		
	4-31G[d]	1.529	1.083	107.7		
	6-31G*	1.528	1.086	111.2		
6, D_{3h}	STO-3G[d]	1.548	1.086	107.8		
	4-31G	1.541	1.082	111.6		
	6-31G*	1.541	1.085	111.7		
7, D_{2h}	STO-3G	1.855	1.066	115.4	1.268	43.0
	4-31G	1.841	1.062	115.6	1.286	44.3
	6-31G*	1.803	1.066	115.7	1.268	44.7
8-D_{4h}	STO-3G	1.849	1.043	180.0	1.323	46.7
	4-31G	1.841	1.058	180.0	1.374	48.0
	6-31G*	1.789	1.065	180.0	1.338	48.1

[a] Bond lengths in Å, angles in degrees. [b] Hydrogen in terminal position. [c] Hydrogen in bridging position. [d] L. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, 93, 808 (1971).

existing. The $1b_{2g}$ HOMO of **7** (D_{2h}) has π^* antibonding carbon–carbon character.[7] Furthermore, no bonding interaction is possible with either the bridging or the other hydrogens since all of them lie in nodal planes. The even more extreme structure **8** (D_{4h}), which has four bridging hydrogens and a doubly degenerate antibonding (e_g) HOMO, is 437 kcal/mol (MP2/6-31G*//6-31G*) less stable than ethane (**5**). In contrast, a geometrically similar D_{4h} C_2Li_6 quadruply lithium-bridged structure is only a few kcal/mol less stable than the global minimum.[21]

What is the reason for the pronounced difference between the bridging proclivities of hydrogen and lithium? C–Li bonds have considerable ionic character. It is favorable electrostatically to position Li^+ cations centrally with regard to both negative charges of a CH_2^-–CH_2^- dianion. However, we have also emphasized the multicenter covalent nature of lithium compounds.[10] Bridging lithium utilizes its p orbitals (not available to hydrogen), e.g., to help stabilize structure **2**. The $1b_{3g}$ HOMO of **2**, shown in Figure 2,[22] illustrates such involvement of the lithium p orbitals. However, the C–C antibonding π^* character of this orbital and the lack of C–H bonding are unfavorable. In the slightly more stable partly bridged structure **1**, carbon–carbon bonding increases, as is shown by the overlap populations in Table VII. The C–C antibonding π^* character of **2** is relieved slightly in **1** since the two carbon p orbitals are tilted in a conrotatory fashion. Figure 3a, drawn with higher contour levels (0.2 au), shows this tilting clearly. Figure 3b was drawn with lower contour levels (0.05 au) to bring out the lithium orbitals.[22] The percent of carbon s character involved in C–Li bonding (as deduced from the localized orbitals)[23] increases from only 0.5% in **2** to 20.8% in **1**. In **1** there is also some σ bonding between lithium and the vicinal hydrogens, as indicated by the overlap population (0.037, 6-31G*) and the

(21) A. J. Kos, D. Poppinger, and P. v. R. Schleyer, *Tetrahedron Lett.*, **21**, 2151 (1980). For a quadruply hydrido bridged rhenium dimer, see R. Ball, W. E. Carroll, R. J. Teller, and T. F. Koetzle, *J. Am. Chem. Soc.*, **99**, 3872 (1977). For an MO analysis of this complex, see A. Dedieu, T. A. Albright, and R. Hoffmann, *ibid.*, **101**, 3141 (1979).

(22) Professor W. L. Jorgensen kindly provided the program (now available as QCPE No. 340) to draw the molecular orbitals. See W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, 1973.

(23) S. F. Boys, "Quantum Theory of Atoms, Molecules, and the Solid State", R. O. Löwdin, Ed., Interscience, New York, 1967, p 253.

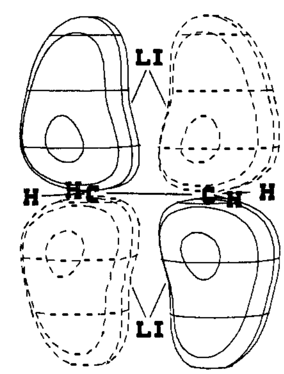


Figure 2. HOMO ($1b_{3g}$) of **2** drawn at a contour level of 0.05 au.

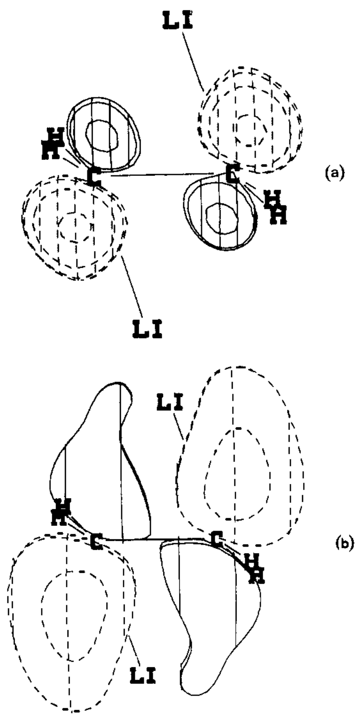


Figure 3. HOMO ($5a_g$) of **1** drawn at contour levels of 0.2 au (a) and 0.05 (au) (b).

lithium–hydrogen distance, 2.310 Å (4-31G). However, this is a much smaller effect than in *trans*-1,2-dilithioethylene, where the vicinal Li–H distance is 2.003 Å (4-31G) and the Li–H overlap population is 0.082 (6-31G*).[10]

In C_2Li_6,[21] lithium–lithium bonding is an important structure-determining factor. Increased lithium–lithium bonding also contributes to the stability of the cis doubly bridged transition state **3'**. The Li–Li distance, 2.392 Å (4-31G), is much shorter than in Li_2, 2.816 Å (4-31G). (However, the Li–Li overlap population in **3'**, 0.247 (6-31G*), is smaller than in Li_2, 0.770 (6-31G*). In our experience, there is no direct relationship between Li–Li distances and overlap populations.) In **4** the lithiums cannot use their p orbitals to form a multicenter bond as favorably.

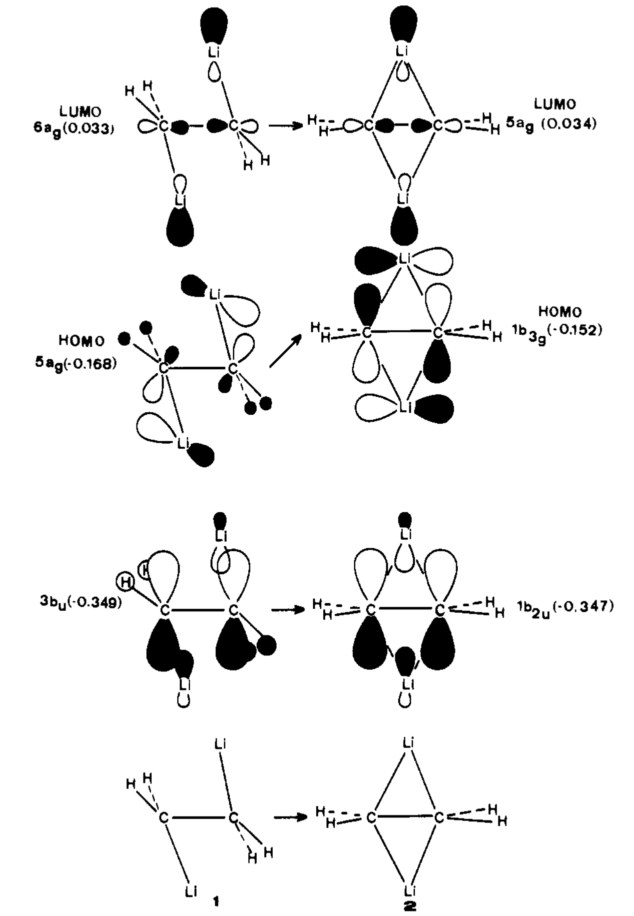


Figure 4. Orbital correlation diagram for the rearrangement 1 → 2: orbital energies (6-31G*) in parentheses.

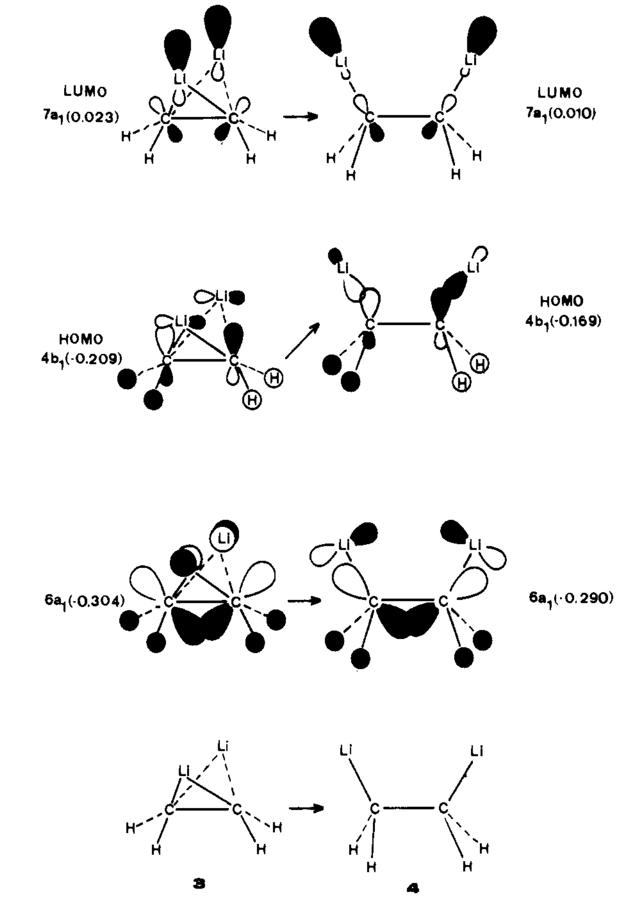


Figure 5. Orbital correlation diagram for the rearrangement, 3 → 4: orbital energies (6-31G*) in parentheses.

The sum of the overlap populations in 4 between lithium, C_α, and C_β, 0.667 (6-31G*), is the lowest among all the isomers (compare 0.744 in 3, 0.816 in 2, and 0.821 in 1).

As we so often have found, lithium prefers geometries which are energetically inaccessibly high for the hydrogen analogs. As pointed out by Reetz[8] and by Hoffmann,[7] the availability of p orbitals in the migrating groups stabilizes dyotropic rearrangement transition states and transforms formally symmetry-forbidden reactions (e.g., for hydrogen) into symmetry-allowed processes. Figure 4 shows an orbital correlation diagram for the rearrangement 1 → 2. The isomerization of 3 into 3′ is also allowed since the orbital nodal properties do not change. The same is true for the conversion of 3′ into eclipsed 4 (Figure 5).

Internal Rotation

Radom, Stiles, and Vincent[11] examined the torsional potential surface of $LiCH_2CH_2Li$ using standard bond lengths and bond angles (4-31G//STD). We extended this study by including more rotational angles (Table III) and were able to locate a very shallow gauche minimum at ϕ = 92.2° (Figure 1a).

The torsional potential surface calculations were then repeated by selecting various LiCCLi dihedral angles and fully optimizing all other geometrical variables. The computationally more efficient 3-21G basis was chosen for this purpose (Figure 1b). In order to compare the two results, the energy lowering at ϕ = 0° in going from 4-31G//STD (Table IV) to 4-31G//4-31G (Table I), 6.4 kcal/mol, was used as the 3-21G//3-21G reference point to construct Figure 1. Although 4-31G and 3-21G values are not strictly comparable, the relative energies should be similar (see Table II). Figure 1 illustrates the dramatic energy lowerings due to optimization. This is greatest (16.4 kcal/mol, 4-31G//STD vs. 4-31G//4-31G) at ϕ = 180°.

The 3-21G//3-21G torsional potential curve shows a more pronounced gauche minimum (3) at ϕ = 84.0° lying 8 kcal/mol (Table II) higher than the global minimum, 1 (ϕ = 180°). A small 3 → 1 potential barrier, about 1.5 kcal/mol (Table IV), is found at ca. ϕ = 100°. The barrier via 4 (ϕ = 0°) is much higher (Table II).

Using the usual Fourier expansion of the torsional potential,[11] the following constants (3-21G//3-21G) were evaluated by least-squares treatment (in kcal/mol): V_1 = -26.43 (4-31G//STD = -13.02), V_2 = -4.30 (-4.75), and V_3 = -2.21 (-3.97). The larger energy gain due to bridging in 1 is responsible for the pronounced difference in the V_1 potentials, which reflect the large dipole interaction term. Analysis of the other terms has been given by Radom et al.[11]

Stability of 1,2-Dilithioethane

Using energy data at the highest theoretical level employed (MP2/6-31G*//3-21G),[10,24,25] the stability of 1 toward possible dissociation models, eq 1-3, was examined. The reaction energies

$$LiCH_2CH_2Li\ (\mathbf{1}) \rightarrow CH_2{=}CH_2 + Li_2 \qquad -1.5\ \text{kcal/mol} \tag{1}$$

$$LiCH_2CH_2Li\ (\mathbf{1}) \rightarrow CH_2{=}CHLi + HLi \qquad +29.3\ \text{kcal/mol} \tag{2}$$

$$LiCH_2CH_2Li\ (\mathbf{1}) \rightarrow trans\text{-}CHLi{=}CHLi + H_2 \qquad +32.7\ \text{kcal/mol} \tag{3}$$

refer to isolated species (e.g., those in the gas phase). Monomeric 1,2-dilithioethane should thus be marginally unstable thermodynamically toward dissociation into ethylene and Li_2, but stable toward the loss of lithium hydride or of hydrogen. The heat of formation of gaseous Li_2 is 50.4 kcal/mol,[26] well above that of

(24) The total MP2/6-31G*//3-21G energies (in au) for the additional species used to evaluate eq 1-9 are: CH_4, -40.332 55; CH_3Li, -47.162 07; C_2H_3Li, -85.124 54; C_2H_4, -78.284 10; C_2H_5Li, -86.318 10; C_2H_6, -79.494 51; HLi, -7.995 96; H_2, -1.137 63; and Li_2, -14.885 43.

(25) As eq 1-3 are not isodesmic, correlation effects are important.

Table VII. Overlap Populations for $C_2H_4Li_2$ Isomers, 6-31G* Basis Set

molecule	C-C	C_α-Li	C_β-Li	C-H	Li-Li	Li-H	% 2s character in the CLi bond[a]	
							C	Li
1, C_{2h}	0.273	0.574	0.247	0.747	−0.148	0.037	20.8	27.0
2, D_{2h}	0.206	0.408	0.408	0.760	−0.198	0.008	0.5	18.7
3′, C_{2v}	0.209	0.372	0.372	0.700	0.247	−0.005	31.0	17.9
4, C_{2v}	0.599	0.744	−0.077	0.735	0.001	−0.000	13.8	89.7

[a] Obtained from molecular orbitals localized according to Boys' procedure.[23]

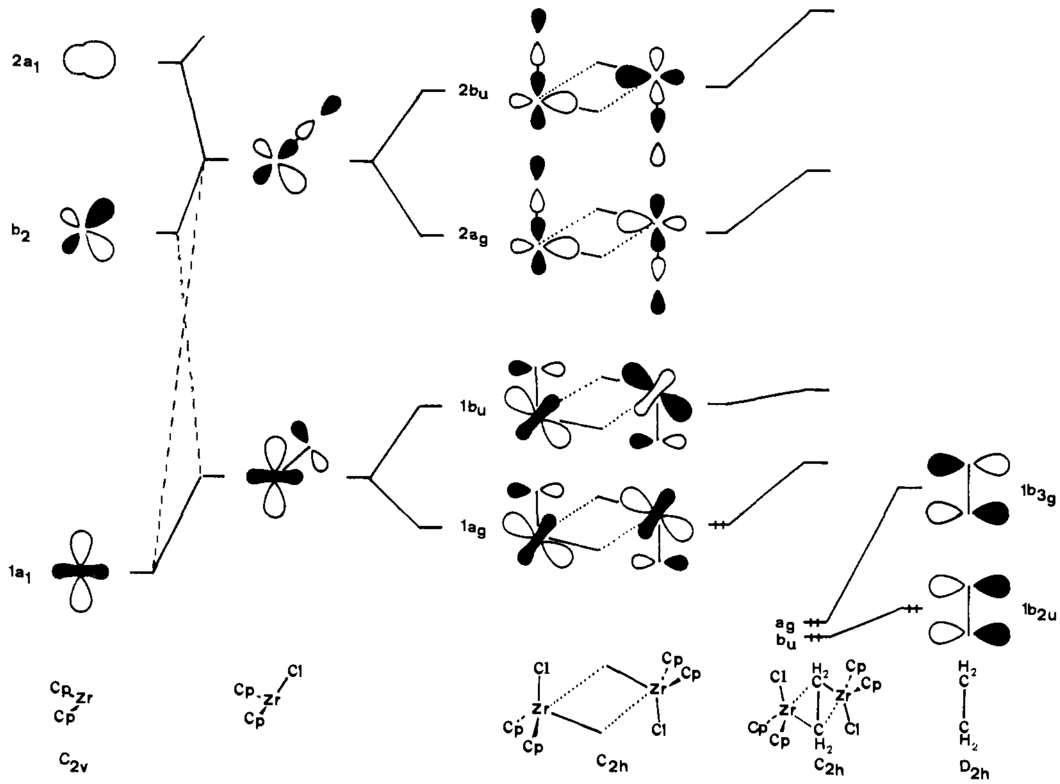


Figure 6. Orbital interaction diagram for **10**.

lithium metal; therefore, the value of −1.5 kcal/mol would become more negative if eq 1 were based on lithium in a higher state of aggregation. However, $C_2H_4Li_2$ will also be stabilized by association (see below) and, in solution, by solvation, so that a final conclusion regarding the thermodynamic stability of 1,2-dilithioethane in condensed states cannot be reached.

By way of comparison, methyllithium monomer also is indicated (MP2/6-31G*//3-21G) to be thermodynamically unstable toward loss of Li_2 and formation of ethane (eq 4). Ethyllithium monomer,

$$2CH_3Li \rightarrow C_2H_6 + Li_2 \quad -35.0\ \text{kcal/mol} \quad (4)$$

like **1**, should also be stable toward elimination of HLi[27] and of H_2 (eq 5 and 6). According to isodesmic eq 7–9, there is an

$$CH_3CH_2Li \rightarrow CH_2{=}CH_2 + HLi \quad +23.9\ \text{kcal/mol} \quad (5)$$

$$CH_3CH_2Li \rightarrow CH_2{=}CHLi + H_2 \quad +35.1\ \text{kcal/mol} \quad (6)$$

$$CH_4 + LiCH_2CH_2Li\ (\mathbf{1}) \rightarrow CH_3CH_2Li + CH_3Li \quad +12.3\ \text{kcal/mol} \quad (7)$$

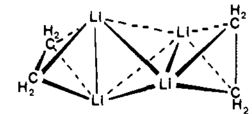
$$2CH_4 + LiCH_2CH_2Li\ (\mathbf{1}) \rightarrow CH_3CH_3 + 2CH_3Li \quad +8.6\ \text{kcal/mol} \quad (8)$$

$$C_2H_6 + LiCH_2CH_2Li\ (\mathbf{1}) \rightarrow 2CH_3CH_2Li \quad +16.0\ \text{kcal/mol} \quad (9)$$

unusually large stabilizing 1,3-interaction between the lithium atoms in **1**.[28] (The earlier study[11] concluded that this 1,3-interaction (eq 9) was destabilizing, but this was due to the use of standard geometries which are very unfavorable energetically.) The stabilization is due to multicenter bonding utilized by the bridging lithiums.[9,10,21]

Dimerization

In dilithioethane aggregates, stabilization due to lithium–lithium interactions might result in species which are stable toward loss of Li_2. Since high-level ab initio calculations on dimers or higher oligomers of dilithioethane are impracticable, we used the semiempirical MNDO method[17] to examine several dimer geometries. The best energy was obtained for structure **9**, the dimer



9, D_{2d}

of **3**. This corresponds to a distorted lithium tetrahedron to which perpendicular H_2CCH_2 units are bound on opposite edges.

The calculated MNDO heats of formation for **1** (−4.2 kcal/mol), **3** (−7.4 kcal/mol),[29] and **9** (−116.2 kcal/mol) indicate a large

(26) D. R. Stull and H. Prophet, "JANAF Thermochemical Tables", 2nd ed., NSRDS, 1971.

(27) M. T. Reetz and W. Stephan, *Tetrahedron Lett.*, 2693 (1977); *J. Chem. Res., Synop.*, **44** (M), 0583 (1981).

(28) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, **95**, 693 (1973).

(29) Evaluation of eq 1 by means of known thermochemical data[26] leads to an expected heat of formation for 1,2-dilithioethane of about 64.4 kcal/mol. This confirms the tendency of MNDO with the current parameterization[17] to overestimate the carbon-lithium bond strength by about 30 kcal/mol.

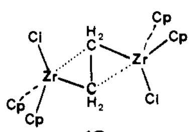
dimerization energy, 101 kcal/mol. This value may be overestimated by MNDO,[29] but aggregates of dilithioethane are certainly expected to be much more stable than the monomer.

Triplet States of 1,2-Dilithioethane

All bonding orbitals in electron-deficient lithium compounds are not occupied. Thus triplet states are often readily accessible.[10] Geometry optimization of the triplet state of the partly bridged structure **1** leads to the symmetrical bridged **2**. Triplet **3′** was found to be lowest in energy. The well-known[10] overestimation of triplet relative to singlet stabilities at the Hartree–Fock level is partly corrected using second-order Møller–Plesset theory. At UMP2/4-31G//4-31G, triplet **3** is 17 kcal/mol less stable than singlet **1**. We thus believe 1,2-dilithioethane to be a ground-state singlet. The MNDO results[17] agree with this conclusion.

Transition Metal Analogues

The vast majority of elements in the periodic table are metals. Lithium, the first such element, can be expected to exhibit structural features which should be common to other metals. A remarkable analogy is found between the zirconio-ethylene complex **10**,[6] with ZrCC angles of 75.9° (X-ray), and **1**, with LiCC angles of 73.3° (4-31G).



10

Following the analysis of Hofmann and Stauffert[30] for complexes involving Cp_2MCl fragments, we can consider **10** to result from the interaction of two $Cp_2MCl{\cdot}AlR_3$ fragments with ethylene. The orbital interaction diagram (Figure 6) shows how the relevant a_g and b_u orbitals of the two metal fragments (Figure 6, middle) are derived from the $1a_1$ and b_2 Cp_2Zr fragment orbitals after interaction with chlorine (Figure 6, left side). The $1b_{2u}$ and $1b_{3g}$ orbitals of ethylene (Figure 6, right side) interact with the $1b_u$ and $1a_g$ orbitals of the metal fragment combination to produce two new stabilized orbitals (b_u and a_g) which are occupied by four electrons (the two π electrons of ethylene and the one extra electron from each of the two zirconium fragments).

In **10**, the distortion from the symmetrical bridged structures results from a gain in energy due to interaction of the ethylene $1b_{3g}$ ($1b_{2u}$) orbitals with the $2a_g$ ($1b_u$) fragment orbital. This interaction is not possible in the symmetrical bridged structure. The distortion in **1** has similar causes. Thus, both 1,2-dilithioethylene and **10** are electron-deficient compounds whose unusual bent geometries result from additional interactions of formally unoccupied lithium and metal fragment orbital with the occupied orbitals of C_2H_4.

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(30) P. Hofmann and P. Stauffert, submitted for publication. See J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 1729 (1976).

A Theoretical Study of the Core Binding Energies of Ozone and Oxygen Difluoride

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Abstract: The core binding energies of O_3 and OF_2 have been calculated as the difference between the total Hartree–Fock energies of the hole states (core electron missing) and the neutral ground states. The results are compared with experimental values. The agreement is very good except for the central oxygen of ozone. The trends in binding energies, as they reflect the bonding in the two molecules, are discussed in terms of the σ and π contributions.

The recent experimental study of core ionization in ozone[1] has produced two interesting results: a large splitting between the terminal and central oxygens of 4.7 eV and the highest O_{1s} binding energy ever reported in the gas phase, 546.2 eV, which is 1 eV higher than that of OF_2.[2] This would imply that the central oxygen atom of O_3 is more positively charged than that of OF_2, despite the more electronegative nature of F. In an attempt to reproduce these results theoretically and hence obtain a better understanding of bonding in ozone, Noodleman (Banna et al.[1]) performed $X\alpha$ scattered wave calculations on the ground states, core-hole states, and "transition states" (obtained by removing half a core electron from the neutral molecule) for both O_3 and OF_2. The $X\alpha$ method proved satisfactory in predicting the splitting, giving 5.1 eV when the binding energies were calculated as the difference between the total energy of the ion with a core hole and the total energy of the neutral molecule ("ΔSCF" method). However, the absolute binding energy was some 6 eV too high for both the OF_2 and the O_3 oxygen atoms.

Table I. Computed Total Energies (hartrees)

O_3	
neutral	−224.2177
central O_{1s} hole state	−204.0835
terminal O_{1s} hole state	−204.3165
OF_2	
neutral	−273.4763
O_{1s} hole state	−253.4321
F_{1s} hole state	−247.9557

We report here the first ab initio SCF calculations of these properties. The molecular orbitals obtained are used to perform separate population analyses for σ and π orbitals, thus providing a more detailed picture of bonding than is possible on the basis of the total populations reported previously for O_3[3] and OF_2.[4]

(1) M. S. Banna, D. C. Frost, C. A. McDowell, L. Noodleman, and B. Wallbank, *Chem. Phys. Lett.* **49**, 213 (1977).
(2) J. W. Koepke and W. L. Jolly, *J. Electron Spectrosc.*, **9**, 413 (1976).
(3) S. Rothenberg and H. F. Schaefer III, *Mol. Phys.*, **21**, 317 (1971).

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