The results in Table I lead to a considerably larger value[15,16] for the enthalpy of rearrangement of *sec*-butyl cation to *tert*-butyl than that estimated by Hogeveen and Brouwer[20] and a considerably smaller one for the stabilization of the 2-norbornyl ion. It is not clear how much of these differences lie in the methods or how much in the experimental conditions.

Finally, we wish to draw attention to the fact that impurities (probably SO_2) in one batch of "Spectrograde" SO_2ClF strongly catalyzed the rearrangement of several cations. We are investigating this phenomenon but caution other workers who are presently studying carbonium ions in this solvent.

Acknowledgments. We appreciate the continued interest and encouragement of Professors H. C. Brown, G. A. Olah, M. Saunders, and P. v. R. Schleyer in the course of this investigation. Acknowledgement is made to donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of the research.

References and Notes

(1) Reference 16 should be considered as part 5 of this series; ref 6a is part 4.
(2) G. A. Olah, *Science*, **168**, 1298 (1970).
(3) Subsequent articles will describe completely our methods for low temperature calorimetry in superacid and a variety of checks to authenticate the ionization process. We will also compare our results in several solvents of very low Lewis basicity (nucleophilicity) with gas phase and solvolysis data.
(4) Most measurements were made at −55 °C at RX concentrations from 10^{-4} to 10^{-2} M. A considerable excess (10–20-fold) of SbF_5 relative to RX was used. Except when rearrangements or decomposition occurred, the heats of ionization were relatively insensitive to temperature and concentration ratio.
(5) See J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Can. J. Chem.*, **49**, 1276 (1971), for the probable nature of the ions actually produced by reaction of RX with excess SbF_5.
(6) Previous reports from this laboratory: (a) E. M. Arnett and J. Larsen, *J. Am. Chem. Soc.*, **91**, 1438 (1969); (b) E. M. Arnett and J. Larsen, "Carbonium Ions", Vol. I, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N.Y., 1968. These earlier data were based on the reaction of alcohols with HSO_3F/SbF_5 under conditions where side reactions could not be ruled out. However, they are generally consistent with those reported here and Larsen's work is completely supported by the present results.
(7) H. C. Brown and Min-Hon Rei, *J. Am. Chem. Soc.*, **86**, 5008 (1964).
(8) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7667 (1976).
(9) The following articles from this laboratory demonstrate the ubiquity (but not the necessity) of proportionality or equivalence of $\Delta G°$ and $\Delta H°$ for ionization processes: (a) E. M. Arnett, D. E. Johnston, L. E. Small, and D. Oancea, *Faraday Symp. Chem. Soc.*, **No. 10**, 20 (1975); (b) E. M. Arnett, R. P. Quirk, and J. J. Burke, *J. Am. Chem. Soc.*, **92**, 1260 (1970); (c) E. M. Arnett and J. W. Larsen, *ibid.*, **90**, (792 (1968).
(10) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).
(11) (a) J. J. Solomon and F. H. Field, *J. Am. Chem. Soc.*, **98**, 1567 (1976); (b) R. H. Staley, R. D. Wieling, and J. L. Beauchamp, *ibid.*, **99**, 5964 (1977); (c) J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, Jr., J. L. Beauchamp, and R. W. Taft, *ibid.*, **99**, 5417 (1977).
(12) L. Radom, D. Poppinger, and R. C. Haddon in "Carbonium Ions", Vol. V, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N.Y., 1976.
(13) No such general relationship would be found for ionization of amines. For example, see R. W. Taft in "Proton Transfer Reactions", E. F. Caldin and V. Gold, Ed., Chapman and Hall, London, 1975, p 45.
(14) The controversey has been brought to a sharp focus by the recent publication, "The Nonclassical Ion Problem", by H. C. Brown with (critical) comments by P. v. R. Schleyer, Plenum Press, New York, N.Y., 1977. See also P. D. Bartlett, "Nonclassical Ions", W. A. Benjamin, New York, N.Y., 1965, and G. A. Olah, *Acc. Chem. Res.*, **9**, 41 (1976).
(15) This comparison is a more appropriate one for the present case than that for the heat of isomerization (−14.5 kcal/mol) of secondary butyl cation to *tert*-butyl cation[14] reported by us previously[16] and confirmed herein by independent results in Table I for generation of *tert*-butyl cation at −25 °C from *sec*-butyl chloride and generation of *sec*-butyl ion at −75 °C.
(16) E. W. Bittner, E. M. Arnett, and M. Saunders, *J. Am. Chem. Soc.*, **98**, 3734 (1976).
(17) This value agrees perfectly with one estimated indirectly by Hazeltine, Wong, and Sorensen, *Can. J. Chem.*, **53**, 1891 (1975), and is close to the value (6.5 kcal/mol) estimated by Brown (private communication) from analysis of solvolysis data.
(18) The actual presence or absence of σ bridging in the 2-norbornyl cation is a structural question and cannot be resolved by kinetic or thermodynamic methods which are, however, essential for defining the importance of the effect in terms of reactivity. Olah[2] has presented a broad range of spectroscopic evidence in support of a σ-bridged structure for the 2-norbornyl ion. Brown and Schleyer differ from each other in evaluation of these results.[14]
(19) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970.
(20) H. Hogeveen, *Adv. Phys. Org. Chem.*, **10**, 29 (1973); D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, **9**, 179 (1972).

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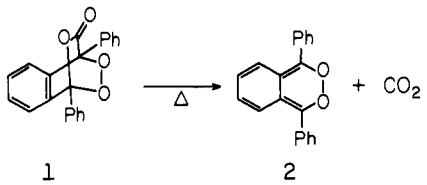
Detection and Trapping of a Chemiluminescent *o*-Xylylene Peroxide. Chemical Light Formation Along Two Separate Paths

Sir:

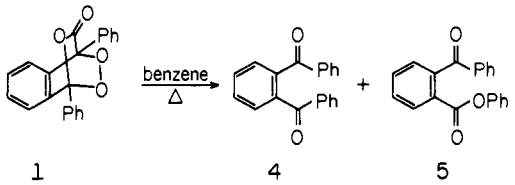
The thermal chemistry of organic molecules containing an oxygen–oxygen bond is usually dominated by reactions involving homolytic or heterolytic cleavage of the peroxide linkage.[1] In this report we would like to describe our observation of a novel retrocycoaddition pathway for thermolysis of pyranone endoperoxide **1** to generate *o*-xylylene peroxide **2** (eq



(1)

1).[2] This is the first reported characterization of this interesting ring system. We have also found that thermolysis of the *o*-xylylene peroxide is chemiluminescent. There are two separate reaction pathways leading to light generation for this molecule. In the absence of an easily oxidized substrate, *o*-xylylene peroxide **2** rearranges to generate electronically excited *o*-dibenzoylbenzene (**4**). In this case chemiluminescence is detected following energy transfer to a suitable emitting energy acceptor, such as biacetyl. The second chemiluminescent path occurs in the presence of any one of several easily oxidized aromatic hydrocarbons. In this case, *o*-xylylene peroxide **2** undergoes a bimolecular reaction resulting in the generation of the fluorescent singlet state of the aromatic hydrocarbon. The mechanism for light formation under these conditions is apparently that which we have recently identified as chemically initiated electron-exchange luminescence.[3]

Photooxidation of 1,4-diphenyl-2-benzopyran-3-one[4] (**3**) in acetone at 0 °C with methylene blue as sensitizer results in the isolation of endoperoxide **1** as a white crystalline solid (mp 105 °C) in 60% yield.[5] This compound is stable in crystalline form at room temperature. Peroxide **1**, however, is completely decomposed when subjected to refluxing benzene for 6 h. The products isolated from this reaction are *o*-dibenzoylbenzene (**4**) and phenyl (*o*-benzoyl)benzoate (**5**) in 85 and 5% yield, respectively.[6]



(2)

Importantly, it is observed that, when the thermolysis of **1** (eq 2) is carried out in rigorously deoxygenated solvent, a deep yellow color develops in the solution as the reaction progresses. The yellow intermediate shows a maximum in its absorption spectrum at 410 nm that tails out to 430 nm. Also, this intermediate is rapidly decolorized by the addition of oxygen to the reaction solution. When the thermolysis of **1** is carried out in

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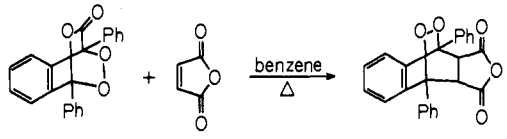
the presence of excess maleic anhydride, the yellow intermediate is not observed, the yield of *o*-dibenzoylbenzene is much reduced, and the yield of ester **5** is essentially unchanged.[7] The major product of the reaction under these conditions is identified as the Diels–Alder adduct (**6**) (eq 3) of maleic anhydride with **2**. Adduct **6** is isolated as a crystalline solid in 70% yield.[8]



(3)

These observations are entirely consistent with the formation of *o*-xylylene peroxide **2** by retro-Diels–Alder loss of CO_2 as the major reaction path for **1**. Compounds containing the *o*-xylylene moiety have recently been characterized in the absence of oxygen under relatively mild conditions.[9] The absorption spectra of these related compounds and the observed chemistry are similar to that which we have found for the intermediate in the thermal reaction of **1**.

Apart from the exciting chemistry involved in the formation, reactions, and properties of **2**, this *o*-xylylene peroxide represents an example of a potentially important new class of chemiluminescent reagents. Thermolysis of **1** in a photon-counting apparatus at 92 °C does not produce a detectable luminescence. This result was not unexpected since only inefficient emission is expected from the excited states of *o*-dibenzoylbenzene under these conditions. However, addition of biacetyl to the reaction solution resulted in easily detected phosphorescence from triplet excited biacetyl.[10] Moreover, it is also observed that addition of rubrene, perylene, or any one of several easily oxidized aromatic hydrocarbons results in readily detected luminescence. The luminescence in this case corresponds to fluorescence from the added aromatic hydrocarbon singlet excited state. The intensity of the chemiluminescence in all cases is directly proportional to the concentration of endoperoxide **1** at constant acceptor concentration.

Our observation of the chemiluminescence from **1** implicates the *o*-xylylene peroxide **2** as the chemiluminescent precursor.[11] In particular, addition of maleic anhydride to a chemiluminescing solution of **1** and perylene quenches the chemiluminescence without affecting the rate of consumption of endoperoxide **1**.[12]

The energy stored in *o*-xylylene peroxide **2** must ultimately appear as the energy of electronic excitation on the added emitter. We have found that there are two kinetically and spectroscopically distinguishable mechanisms operating to transform the potential energy of *o*-xylylene peroxide **2** to an excited state of the emitter. In the first, examplified for biacetyl, endoperoxide **1** loses CO_2 to form **2**, which in a subsequent surprisingly slow unimolecular rearrangement forms electronically excited *o*-dibenzoylbenzene (**4**). Energy transfer from excited ketone **4** to biacetyl results in the formation of the observed emitting triplet state of biacetyl. It should be noted that stretching the peroxide bond of planar **2** to form ketone **4** is a process which would result in generation of a high energy doubly excited state.[11] Consistent with this mechanistic interpretation we observe classical consecutive reaction kinetics, shown in Figure 1, for the buildup and decay of chemiluminescence emission intensity under these conditions. This mechanism for light generation is shown as path A in Scheme I.

The second route leading to light emission occurs in the presence of any one of several easily oxidized aromatic hydrocarbons (ArH) and is an example of the general excitation mechanism we have recently identified as chemically initiated electron-exchange luminescence. The initial interaction between *o*-xylylene peroxide **2** and ArH in this case is an electron

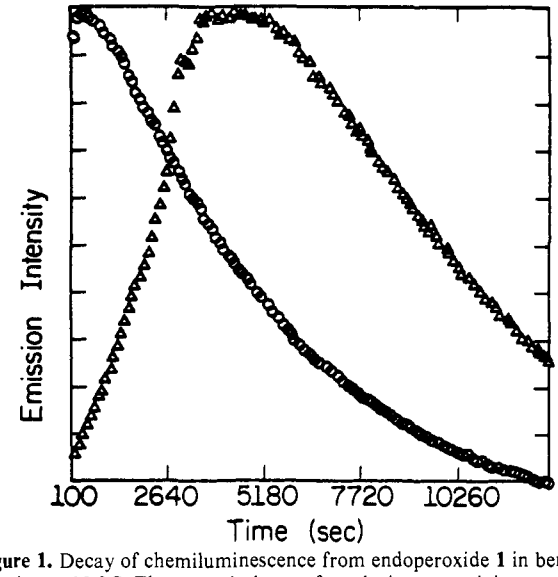
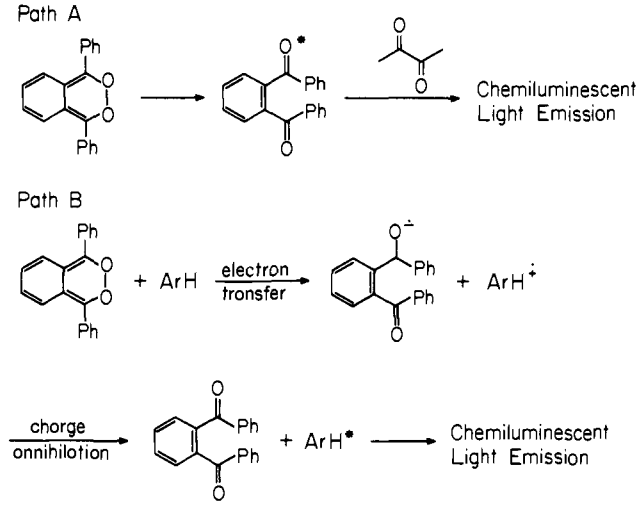


Figure 1. Decay of chemiluminescence from endoperoxide **1** in benzene solution at 92 °C. The open circles are for solutions containing perylene, the open triangles are for biacetyl-containing solutions.

Scheme I



transfer from ArH to the peroxide. Subsequent ring opening of the reduced peroxide followed by annihilation of the resulting radical ions generates the observed products, *o*-dibenzoylbenzene and electronically excited aromatic hydrocarbon, as is shown in path B of Scheme I. Evidence that this path is operating comes from the observation that the singlet excited state of ArH is efficiently formed under conditions where energy transfer from singlet **4** is highly improbable. Also, the efficiency of light production is inversely proportional to the one-electron oxidation potential of ArH indicating an electron transfer as a key step in the excitation sequence. Finally, the kinetic behavior of the light intensity in the presence of ArH, shown in Figure 1, indicates that the rate of reaction of the intermediate *o*-xylylene peroxide **2** has been increased by the addition of ArH so that the formation of **2** from endoperoxide **1** is now rate determining.

In summary, we have observed a novel thermal reaction of pyranone endoperoxide **1** to form the unique *o*-xylylene peroxide **2**. This peroxide represents one of the few known or postulated vinyl peroxides. In addition, *o*-xylylene peroxide **2** reacts along two distinct paths to produce chemiluminescent emission. These observations may be extrapolated to the much studied isoelectronic luminol system in which intramolecular electron exchange is possible. We are continuing to investigate the interesting and novel chemical and chemiluminescent reactions of endoperoxide **1** and related systems.

Acknowledgment. We thank Professor Michl of the University of Utah for helpful discussions. This work was supported in part by the Office of Naval Research and in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

References and Notes

(1) For leading references, see "Organic Peroxides", D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1970.
(2) The systematic name for this compound is 1,4-diphenyl-2,3-benzodioxin. We prefer to use the trivial name that identifies **2** as containing both an *o*-xylylene moiety and a peroxide linkage.
(3) J. Y. Koo and G. B. Schuster, *J. Am. Chem. Soc.*, **99**, 6107 (1977).
(4) J. M. Holland and D. W. Jones, *J. Chem. Soc. C*, **530** (1970). In this paper the pyranone was reported to take up O_2 in the dark; the peroxide that results in that circumstance is probably a polymer.
(5) The endoperoxide was characterized as follows: IR ($CHCl_3$) 2950, 1785, 1525, 1460, 1330 cm^{-1}; ^1H NMR ($CDCL_3$, internal Me_4Si) δ 6.8–7.0 (m, 2 H), 7.2–7.9 (m, 12 H); ^{13}C NMR ($CDCl_3$), internal Me_4Si) δ 166, 136 130.8, 130.2, 129.6, 129.3, 128.8, 128.2; mol wt (osmometry) required 330, found 328 ± 4; active oxygen contents, 87 ± 10% of theoretical. Anal. Calcd for $C_{21}H_{14}O_4$: C, 76.36; H, 4.24. Found: C, 76.36; H, 4.27.
(6) These compounds were identified by comparison with authentic samples. The *o*-dibenzoylbenzene was prepared according to F. R. Jensen, *J. Org. Chem.*, **25**, 269 (1960), and the phenyl (*o*-benzoyl)benzoate according to F. F. Blicke and R. D. Swisher, *J. Am. Chem. Soc.*, **56**, 902 (1934).
(7) This observation is consistent with formation of **2** and **5** along parallel paths from **1**.
(8) The adduct was characterized as follows: IR ($CHCl_3$) 2980, 1870, 1690, 1600, 1490 cm^{-1}; ^1H NMR ($CDCl_3$, internal Me_4Si) δ 7.0–7.85 (m, 14 H), 4.1 (s, 2 H); mol wt (osmometry) required 384, found 381 ± 5; active oxygen content, 94.4 ± 6% of theoretical. Anal. Calcd for $C_{24}H_{18}O_5$: C, 74.99; H, 4.20. Found: C, 74.65; H, 4.28. The stereochemistry of **6** is not yet known.
(9) Leading references: (a) K. L. Tseng and J. Michl, *J. Am. Chem. Soc.*, **99**, 4840 (1977); (b) W. R. Dolbier, Jr., K. Matsui, J. Michl, and D. U. Horak, *Ibid.*, **99**, 3876 (1977); (c) E. Chacko, J. Bornstein, and D. J. Sardella, *Tetrahedron Lett.*, 1095 (1977); (d) R. D. Miller, J. Kolc, and J. Michl, *J. Am. Chem. Soc.*, **98**, 8510 (1976); (e) D. S. Weiss, *ibid.*, **97**, 2550 (1975).
(10) The triplet and singlet energy of *o*-dibenzoylbenzene is above that of biacetyl: G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).
(11) In a recent review Michl has suggested, based on theoretical considerations, that an *o*-xylylene peroxide is the key chemiluminescent intermediate in the light-forming reaction of luminol: J. Michl, *Photochem. Photobiol.*, **25**, 141 (1977), and references cited therein.
(12) Typical conditions. [**1**] = 5×10^{-4} M, [perylene] = 2×10^{-4} M, [maleic anhydride] = 1×10^{-3} M in benzene at 92 °C. Maleic anhydride will not significantly quench perylene singlets under these conditions.
(13) Fellow of the Alfred P. Sloan Foundation 1977–1979.

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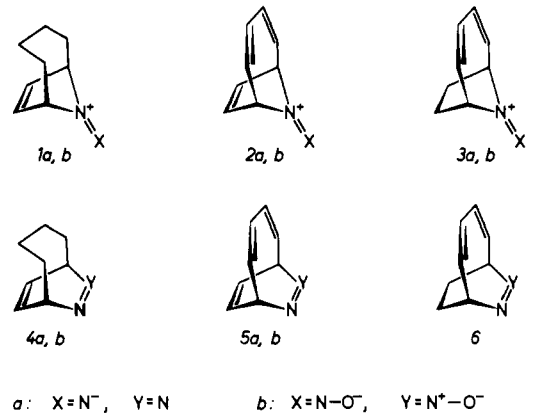
Bis-Pericyclic Reactions: Retrocycloaddition and the Importance of Avoiding Piecewise Analysis[1]

Sir:

Qualitative applications of orbital symmetry conservation rules often focus on the number of electrons delocalized about a monocyclic atomic array in the transition state of a concerted reaction. Thus a thermal transformation is designated "allowed", if the total number of $(4q + 2)_s$ and $(4r)_a$ components is odd.[2] Equivalently this requirement is met for (4M + 2) and (4N) electron transition states, if an arbitrary set of atomic orbital constituents is isoelectronic with the appropriate "Hückel"/"aromatic" or "Möbius"/"aromatic" arrangements, respectively.[3,4] Within this conceptual framework it is natural to speculate on the consequences for bis-, tris-, or polykis-pericyclic reactions arising formally by incorporating cycles with opposing electronic effects. Thus a bis-pericyclic, face-to-face cycloaddition which couples a (4N)-forbidden and a (4M +2)-allowed fragment might conceivably experience a kinetic barrier relative to the same reaction lacking the (4N) moiety.

Anastassiou and Yamamoto have recently concluded that the rate of nitrogen extrusion for diazenes **1a-3a** falls in the order **1a** > **2a** > **3a**.[5] The "less efficient" fragmentation for **2a** relative to **1a** was interpreted as caused by the presence of the butadiene bridge in the former. Namely, the corresponding bis-pericyclic transition state is destabilized by a suprafacial (4N) = 8-electron component. Experiments we have conducted with the analogous azoalkanes **4a, 5a,** and **6** do not sustain this supposition. Furthermore we show that evaluation of the bicyclic transition states piecewise[6] leads to illusory predictions which can be sidestepped by a straightforward MO analysis.



It has been shown that treatment of azo *N*-oxides with hexachlorodisilane at 25 °C leads to azoalkanes, if the carbon skeleton is saturated,[8] and to cyclic dienes derived from them, if it is unsaturated.[9] The desired *N*-oxide precursors, **4b** (mp 113–114 °C) and **5b** (mp 82–83 °C), were prepared by basic peroxide, hydrolytic oxidation[9,10] of the corresponding urazole adducts obtained in turn from the cycloaddition of *N*-methyltriazolinedione (MTAD) and cyclooctadiene[10] (COD) and cyclooctatetraene[11] (COT), respectively.[12] Each was dissolved in $CDCl_3$, cooled to −40 °C, and treated with an excess of the silane reagent. The reactions were monitored by NMR between −30 to −40 °C. Over a period of hours the bicycles were converted quantitatively to COD and COT as determined by integration against an internal standard. No signals for an intermediate azoalkane were observed. Clearly nitrogen extrusion is much faster than deoxygenation. At −30 °C no discrimination between the presence or absence of the butadiene bridge is evident. With the exception of a single case,[13] all 1,2-diazacyclohexa-1,4-dienes likewise have gone unobserved at temperatures below −30 °C.[14] Within the experimental limits, the results suggest that the bis-pericyclic process occurs unretarded relative to the simple pericyclic reaction. Complementing the lability of **4a** and **5a** is the behavior of azodiene **6** which can be isolated but decomposes quantitatively at 50 °C to 1,3,5-cyclooctatriene and nitrogen.[15]

The rapid loss of nitrogen from **4a** and **5a** is readily apprehended by considering the fate of the electrons in the bonds to be made and broken in the pericyclic transition state. For both azocycles, the symmetric combination of the C–N bonds (**7**) may be transformed across the potential energy surface for retrocycloaddition into the second π bond of N_2. The antisymmetric union **8** likewise correlates smoothly with the highest lying π_A levels of the cycloalkenes COD (**9**) and COT (**10**). These qualitative and symmetry-sufficient orbital correlations have been confirmed by a complete MO calculation of the decomposition of azotriene **5** to cyclooctatetraene and N_2. The geometry of **5** was obtained by CNDO/B[16] optimization; deazetation, followed numerically by CNDO/B, CNDO/S,[17] and PRDDO.[18] All of the latter produce the result that MO's **7** and **8** in **5** are strongly mixed with fragment orbitals of the same symmetry as expected for a molecule

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