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SYNTHESIS, REACTIONS, AND PHOTOELECTRON SPECTRUM OF 8,11-DIMETHYLENE-PENTACYCLO$[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]$TRIDECANE

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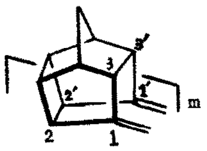
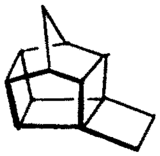
We wish to report the synthesis, reactions, and photoelectron spectrum of 8,11-dimethylenepentacyclo$[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]$tridecane (1), a potential precursor of a derivative of the [2.2.2]propellane[1] (2). Another interesting aspect of 1 is the unique spatial arrangement of its double bonds. The cage structure forces the double bonds to adopt a relative orientation as shown in 1a. A molecular model shows that there may be significant through-space interaction between the p-orbitals on C_1 and $C_{1'}$, with the internuclear distance being about 2.30A°. The interaction of orbitals through space and through bonds has been a subject of considerable interest.[2] A spectroscopic study of the interaction between the two double bonds in 1 was therefore of theoretical and experimental interest.



1

1a



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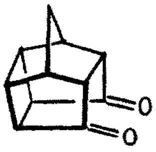

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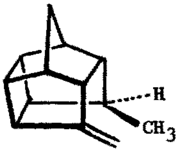

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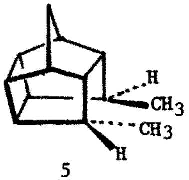

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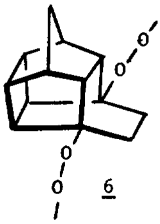
The reaction of diketone 3[3] with two equivalents of methylene triphenylphosphorane[4] in DMSO gave 1 in 50% yield. Compound 1 is a viscous liquid with characteristic olefin odor: fp ~0° C; nmr ($CDCl_3$, 100 MHz) δ1.30 (d,1H, J=10.5 Hz), 1.68 (d,1H, J=10.5 Hz), 2.36 (m,2H), 2.67 (bs, 4H) 2.86 (m,2H), 4.47 (d,2H, J=2.0 Hz), 4.56 (d,2H, J=2.0 Hz); ir (neat), 3030 (C-H), 1675 (C=C), 885 cm^{-1} ($>C=CH_2$). The structure of 1 was further confirmed by the hydrogenation products 4 (80%) and 5 (10%).[5]

Interestingly enough, 1 became an amorphous white powder (m.p. ~ 170°C-decmp.) after standing in air for two weeks. The nmr ($CDCl_3$) of this compound showed broad absorption bands at δ 1.0-2.0 and δ2.0-2.8 with no vinyl proton bands or bands corresponding to O-C-H protons. The average molecular weight was found to be 1140 (osmometry). Combustion analysis indicated a hydrocarbon to oxygen (O_2) ration of 1.1:1.0. Thus, a peroxide copolymer with structure 6 is proposed for this compound. In addition, consistent with the presence of a peroxide function, 6 liberated iodine from hydriodic acid in acetic acid. In contrast to 1, 4 was stable to oxygen. The remarkable reactivity of 1 toward oxygen suggests that these two double bonds have a significant and intriguing interaction.[6]

When 1 was allowed to react with one equivalent of bromine in pentane, compound 8 (via path a in 7, 40%) [($CDCl_3$, 60 MHz), δ1.49 (bs,2H), 1.85 (m,1H), 2.40 (bs,5H), 3.00 (bs,1H), 3.30 (d,1H, J=10.0 Hz, diastereotopic CH_2Br), 3.59 (d,1H, J=10.0 Hz, diastereotopic CH_2Br) 4.21 (bs,1H, CHBr), 4.80 (S,2H); m.p. 50-52°] and 9[7] (via path b in 7,~8%) [($CDCl_3$, 60 MHz), δ 1.35 (d,1H, J=10.5 Hz), 1.76 (d,1H, J=10.5 Hz), 2.50 (S,4H), 2.62 (bs,2H), 2.95 (m,4H), 3.18 (m,2H); m.p. 101°] were obtained. The formation of 8 is formally the result of relieving the strain in intermediate 7. When 9, apparently with the ethylene bridge protons being fortuitously equivalent, was treated with sodium in glyme, the Grob fragmentation[10] product 1 was obtained in ~ 20% yield with no propellane 2 formed. It is noteworthy that, in accord with autoxidation reaction, no 10 was found in the bromination product mixture.



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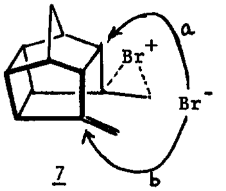

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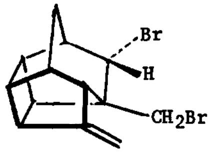

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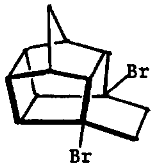

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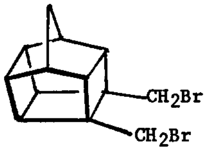

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One of the most powerful tools for studying the interaction between double bonds is the recently redeveloped photoelectron spectroscopy.[8] Thus, the π-ionization potentials of 1 and 4 were measured from photoelectron spectra and are shown in Table I.

Table I

π-Ionization Potentials (eV) of Non-conjugated Dienes Obtained from Photoelectron Spectra

Molecule	I_1	I_2	I_2-I_1
1	8.50	8.90	0.40
4	9.10		
Norbornadiene[a]	8.69	9.55	0.86
Norbornene[a]	8.97		
Bicyclo [2.2.2] Octadiene[a]	8.87	9.45	0.58
Bicyclo [2.2.2] Octene[a]	9.05		

[a] P. Bischof, J.A. Hashmall, E. Heilbronner, and V. Hornung, Helv. Chim. Acta, 52, 1745 (1969). See also: N. Bodor, M.J.S. Dewar, and S. D. Worley, J.Am.Chem.Soc., 92, 19 (1970).

A π-ionization potential of 9.10 eV for 4 was observed (see Table I). In contrast, two such ionizations at 8.50 and 8.90 eV were found in 1. Thus a 0.40 eV splitting characterizes the π-π interaction in 1, with the two bands collapsing into a single π-level in 4. By comparison, norbornadiene and bicyclo [2.2.2] octadiene have π-π splittings of 0.86 and 0.58 eV, respectively. If the dominant mode of interaction was through space (vide infra), the average of the first two π I.P. of a diene should be very close to that of the corresponding "mononene," usually within 0.15 eV. This was shown to be the case for norbornadiene and bicyclo [2.2.2]-octadiene. On the other hand, the mean of the first two π I.P. in 1 was 8.70 eV instead of 9.10 eV. This can be explained in terms of the intervention of through-bond interaction as shown in Fig.1. The through-bond coupling destabilizes the π-S combination, lowering the splitting[9] from the expected 1.20 eV [2 x (9.10-8.50)] to 0.40 eV.

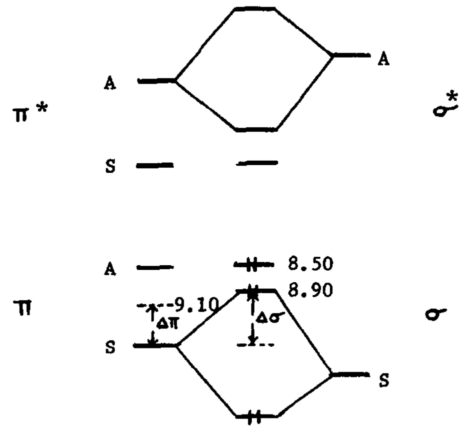

Figure 1. Interaction diagram for 1. π and π^* levels after interaction through space are placed at left, and the σ orbitals (C_2-$C_{2'}$ or C_3-$C_{3'}$) with the correct symmetry to mix with the levels are at right. The symmetry element is the mirror plane defined in 1. Note $\Delta\pi < \Delta\sigma$.

Various attempst to react 1 with dienophiles such as tetracyanoethylene and 1-phenyl-1,3,4-triazoline-2,5-dione (symmetry allowed $\pi 2s + \pi 2s + \pi 2s$ reaction), however, have been unsuccessful. Photolysis of 1 in acetone gave no indication of formation of propellane derivative 2.[10,11]

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References:

1. (a) K. B. Wiberg and G. J. Burgmaier, *J. Am. Chem. Soc.*, **94**, 7396 (1972).
   (b) W.-D. Stohrer and R. Hoffmann, *ibid.*, 779 (1972); M. D. Newton and J. M. Schulman, *ibid.*, **94**, 773 (1972).
   (c) For excellent review on propellane system, D. Ginsburg, *Accounts Chem. Res.*, **2**, 121 (1969); **5**, 249 (1972).
2. R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971); E. Heilbronner and H.-D Martin, *Helv. Chim. Acta*, **55**, 2447 (1972), and references cited therein.
3. R. C. Cookson, E. Crundell, and J. Hudec, *Chem. Ind.* (London), 1003 (1958).
4. R. Greenwald, M. Chaykovsky, and E.J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).
5. Spectral data on these compounds are made available upon request.
6. Norbornadiene, however, does not undergo autoxidation under the same condition.
7. For comparison, 1,4-dibromo-bicyclo[2.2.2]octane shows a singlet at δ2.38. Consistent with the presence of bridge-head bromide, compound 9 is inert to ethanolic AgNO$_3$ solution.
8. D. W. Turner, A. D. Baker, C. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley, London, 1970; C. R. Brundle and M. B. Robin in "Determination of Organic Structure by Physical Method," ed. F. Nachod and J. Zuckerman, Academic Press, New York, 1971, Vol. 3, p. 1.
9. A similar example where both through-space and through-bond coupling are operating has been reported for the boat form of 1,5-cyclooctadiene, see R. Hoffmann, E. Heilbronner, and R. Gleiter, *J. Am. Chem. Soc.*, **92**, 706 (1970).
10. All new compounds gave satisfactory elementary analyses.
11. Recently, a successful synthesis of [2.2.2]propellane system has been reported. P. E. Eaton and G. H. Temme III, 165th ACS National Meeting, Dallas, Texas, April 9, 1973; Abstracts, ORGN 58.