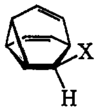
alcohol (58% yield) whose room-temperature nmr spectrum is uniquely consistent with that of fluxional tricyclo[3.3.1.$0^{2,8}$]nona-3,6-dien-9-ol (barbaralol, **7**, X = OH).[18,19] Correspondingly, $LiAlH_4$–$AlCl_3$ reduction[20] of **1b** provided barbaralol (**7**, X = OH, 30%), indan (13%),[17] and barbaralane (**7**, X = H, 30%).[21] **1a** could not be detected.



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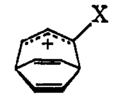
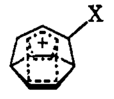


X = H,OH

8a



8b

These facile cationic rearrangements are difficult to reconcile with any hope that the six-π-electron bicyclo[3.2.2]nonatrienyl cation (**8a**) might enjoy the unusual stability suggested by its alternative formulation as a "bicyclotropylium" ion (**8b**), for if one chooses to rationalize these results by invoking an unusually selective nucleophilic capture of a stable **8b**, one is then compelled to predict correspondingly unusual high solvolytic rates for appropriate derivatives of **7**.[23] Since acetolysis of barbaryl tosylate (**7**, X = OTs) is, in fact, a remarkably sluggish reaction,[19] one is led to favor the simpler alternative: **8** possesses *no* unusual stability. In the accompanying communication,[24] any suggestion to the contrary is shown to be incompatible with the theoretical prediction that **8** be "antibicycloaromatic."

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(18) τ^{CDCl_3} 4.12 (t,[8] 7.5), 4.45 (t, 7.5), 5.92 (m), 6.02 (m), 6.38 (t, 3.5), 7.55 (m), and 8.03 ppm (broad singlet vanishing upon D_2O treatment) of relative areas 0.9:0.9:4.5 (5.92 + 6.02):1:2.1:1.1. Lit.[19] τ 4.00 (t), 4.35 (t), 6.02 (d), 6.48 (t), 7.57 (m), and 8.62 ppm (m).

(19) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967). We are grateful to Professor Doering for providing a copy of this manuscript prior to publication.

(20) V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.*, **89**, 1695 (1967).

(21) $\nu_{max}^{CDCl_3}$ 3045, 2950, 2920, 2860, and 1615 cm^{-1}; τ^{CDCl_3} 4.32 (t,[8] 7.5), 5.97 (t, 7.5), 7.63 (m), and 8.93 ppm (t, 2.5), of relative areas 2:4.1:2.8:2.5. Lit.[19] ν_{max} 3045, 2952, 2920, 2862, and 1618 cm^{-1}; τ 4.38 (t, 7.3), 6.10 (t, 7.1), 7.73 (m), and 8.97 ppm (t, 2.5). Lit.[22] 4.37 (t, 7.5), 6.03 (t, 7.5), 7.67 (m), and 8.94 ppm (t, 2.5).

(22) V. Buthan, H. Klusacek, and H. Musso, *Angew. Chem.*, **79**, 152 (1967); *Angew. Chem. Intern. Ed. Engl.*, **6**, 176 (1967).

(23) A. Diaz, M. Brookhart, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3133 (1966).

(24) M. J. Goldstein, *ibid.*, **89**, 6357 (1967).

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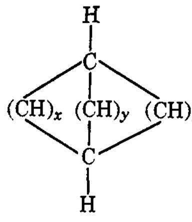
Bicycloaromaticity. The 4*m* + 2, 4*n* Rule

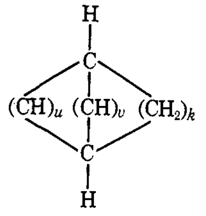
Sir:

The elaboration of π MO theory, and of Hückel's rule in particular, requires a prior segregation of σ and π orbitals. This, in turn, is rigorously permitted only by a planar geometry. It is less clear that experimental manifestations of aromaticity demand this geometry as a prerequisite. With this in mind and stimulated by recent preparative achievements,[1] the author here outlines a π MO treatment of C_mH_m bicyclic hydrocarbons which leads to a simple theoretical rule for anticipating aromaticity, if only when *m* is odd (cations and anions).

π bicycloaromaticity is first defined as the enhanced thermodynamic stability (measured or predicted) of the hydrocarbon **1** in comparison with an appropriate reference compound, one that possesses the same number of trigonal carbons and π electrons. The latter, **2**, is a bicyclic representative of Winstein's bishomoconjugated series[2] chosen such that $u + v = x + y + z$. **k**, the number of methylene groups in **2**, is an experimental parameter wisely adjusted so as to minimize differences between the σ-bond interactions of **1** and **2**.



1



2

$$x + y + z = u + v$$

Following a well-explored sequence of approximations,[3] one recognizes that odd systems (odd *z* in **1**, odd *v* in **2**, all other bridges even) permit the neglect of all bridge–bridge interactions except for that one between the NBMO[4] of $(CH)_z$ or $(CH)_v$ and the HBMO *or* LABMO of the even bridges. Only one of these latter two can possess the same symmetry as does the NBMO (symmetric (S) or antisymmetric (A) with respect to the plane bisecting the bridgehead–bridgehead axis). Its interaction then lowers the lower energy MO of the interacting pair while raising that of the higher one somewhat more.[5]

Bishomoconjugation. As illustration, if $v = 1, 5 \ldots 4q + 1$, the S-NBMO of $(CH)_v$ in **2** must mix with the S-HBMO of $(CH)_u$ whenever $u = 2, 6 \ldots 4r + 2$. The $(u + v - 1)$ π electrons of the cation are then accommodated within $2(q + r) + 1$ BMO's, the highest of which has now been stabilized. The $(u + v + 1)$ π electrons of the corresponding anion must in addition now occupy a (formally antibonding) destabilized MO. Alternatively, if $v = 3, 7 \ldots 4q + 3$, the A-NBMO

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(1) (a) T. S. Cantrell and H. Schechter, *J. Am. Chem. Soc.*, **87**, 3300 (1965); (b) W. Grimme, *Chem. Ber.*, 100, 113 (1967); (c) L. G. Cannell, *Tetrahedron Letters*, 5967 (1966); (d) M. Jones, Jr., and S. D. Reich, *J. Am. Chem. Soc.*, **89**, 3935 (1967); (f) S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *ibid.*, **89**, 3656 (1967); (g) M. J. Goldstein and B. G. Odell, *ibid.*, **89**, 6356 (1967); (h) J. M. Brown, *Chem. Commun.*, 638 (1967).

(2) (a) Footnote 4 in ref 1f. (b) The otherwise convenient term "bishomoaromatic" is here avoided only because the pertinent reference system has not yet been defined. *E.g.*, the computed delocalization energy of 0.386β for the 7-norbornenyl cation[2c] refers to the isolated π bridges. It becomes −0.342β or −0.432β if referred to the allyl or the cyclopropenyl cation. (c) R. J. Piccolini and S. Winstein, *Tetrahedron Suppl.*, **2**, 423 (1963).

(3) (a) M. J. S. Dewar, *Proc. Cambridge Phil. Soc.*, **45**, 639 (1949); (b) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341, 3345 (1952); (c) M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1966); (d) K. Fukui, "Molecular Orbitals in Chemistry, Physics and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1964, p 525; (e) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511, 4388, 4389 (1965).

(4) Abbreviation used: NBMO, nonbonding molecular orbital; HBMO, highest bonding molecular orbital; LABMO, lowest antibonding molecular orbital.

(5) C. A. Coulson, "Valence," 2nd ed, Oxford University Press, London, 1961, p 75, eq 5 with $S > 0$.

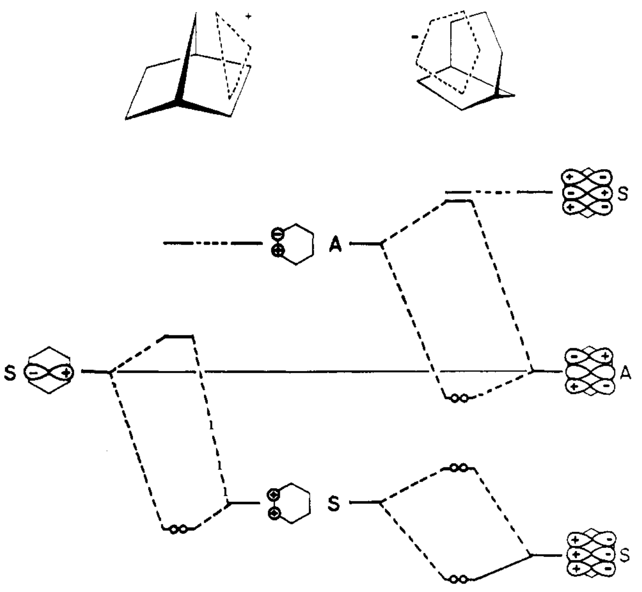

Figure 1. Bridge orbital interactions: the 7-norbornenyl cation and the 4-bicyclo[3.2.1]octa-2,6-dienyl anion.

mixes with the A-LABMO of $(CH)_u$; here the anion is stabilized. The simplest two examples of stabilized ions ($q = r = 0$; *e.g.*, the 7-norbornenyl cation[2c,6] and the 4-bicyclo[3.2.1]octa-2,6-dienyl anion)[1f,1h] are further illustrated in Figure 1.

The four possible combinations of one even and one odd bridge are listed in Table I, whose entries are the charges of the bishomoconjugatively stabilized ions; all contain $4m + 2$ π electrons ($m = q + r$, $q + r + 1$).

Table I. Bishomoconjugatively Stabilized Ions

		u	$4r$	$4r + 2$
		LABMO	S	A
v	NBMO	HBMO	A	S
$4q + 1$	S		−1	+1
$4q + 3$	A		+1	−1

One is less surprised by the conclusion[7] than by its consistency with the meager experimental data now available.[1f,h,6] The approximations used are quite drastic and may well not survive further application to the presumably stable but as yet unknown bicyclo-[4.1.**k**], -[5.4.**k**], and -[6.3.**k**] anions and the bicyclo-[4.3.**k**], -[5.2.**k**], and -[6.1.**k**] cations. In any event, such flaws are expected to cancel when bishomoconjugated ions (**2**) are compared with their isoelectronic counterparts (**1**) of principal concern.

Bicycloaromatics. These are constructed in much the same manner: the $(CH)_x$ and $(CH)_y$ HBMO's and/or LABMO's are mixed with the NBMO of $(CH)_z$. All must be either A or S as defined above.[8] Whenever $x = y$, the four possible combinations of one odd and two even bridges are provided by a table identical in all respects to Table I except that v, u, $4r$, $4r + 2$ are replaced by z, $x + y$, $8r$, and $8r + 4$. Neither the entries nor their significance is changed. If $x \neq y$, the longer bridge dominates since its LABMO and HBMO are closer to the nonbonding level.

One thus easily discovers that *stabilization is achieved whenever the sum of π electrons, provided by the unique odd bridge and one even bridge* (the longer one, if they differ), *equals $4m + 2$* ($m = 0, 1, 2 \ldots$). Despite this similarity to bishomoconjugative stabilization, the second even bridge always contributes significantly, if never quite additively.[9] Such added stabilization should also be greater for identical than for different even bridges. In order that these stabilized ions be bicycloaromatic, however, they must also be isoelectronic with a bishomoconjugatively *destabilized* reference. *Bicycloaromaticity thus further requires that the total number of π electrons equals $4n$.*[10] (Conversely, **1** is conjugatively destabilized if the odd bridge and one even bridge provide $4m$ π electrons and *antibicycloaromatic* if, further, $4n + 2$ π electrons are available from all three bridges.) Examples of the four possible classes of cations and anions are listed in Table II.

Table II. The Simplest Maximally Conjugated C_mH_m Bicyclic Ions[a]

	Stabilized	Stabilized and bicyclo-aromatic	De-stabilized	Destabilized and antibicyclo-aromatic
Cations	4.4.3	2.2.1	4.4.1	3.2.2
	6.4.1	4.3.2	6.4.3	4.2.1
Anions	4.4.1	3.2.2	4.4.3	2.2.1
	6.4.3	4.2.1	6.4.1	4.3.2

[a] Entries are x, y, and z in the conventional (descending) numerical order.

Experimental support for this $4m + 2$, $4n$ rule is, as yet, quite minimal. The stability of the [2.2.1] cation is well known,[6,11] but the behavior of its reference cations [4.1.**k**] or [3.2.**k**] (**1**) is not. Of the potential antibicycloaromatics, the [2.2.1] anion has resisted generation by various brutal means.[12] Reactions that might have led to [3.2.2][1g] and [4.2.1.][13] cations provided only rearranged products.

By implication, this approach precludes appreciable bishomoconjugative stabilization or bicycloaromaticity in any even system. Bicyclo[2.2.2]octa-2,5,7-triene provides a uniquely instructive example. Its π-BMO's are all S, its π-ABMO's all A, and the destabilization thereby anticipated cannot easily be relieved by ring distortion. Appropriately then, hydrogenation of its

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(6) (a) M. Brookhart, A. Diaz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3135 (1966); (b) H. G. Richey, Jr., and R. K. Lustgarten, *ibid.*, **88**, 3138 (1966).

(7) These are obviously perturbed aromatic ions and the arguments above differ only trivially from Dewar's derivation of the Hückel rule.[3a-c]

(8) If $x = y$, a second symmetry plane is possible. Then, the $(CH)_z$ NBMO can mix only with the mutually antisymmetric combination of $(CH)_x$ and $(CH)_y$ orbitals. Nevertheless, since all would have to remain of common A or S symmetry, no energetic consequences are to be expected (within these approximations). Explicit consideration of σ-orbital interactions in the 7-norbornadienyl cation, however, there reveals a destabilizing effect of such added symmetry. *Cf.* R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); *J. Am. Chem. Soc.*, **86**, 1259 (1964).

(9) *E.g.*, in a zero-order Hückel treatment, the stabilization energy of the C_{2v} 7-norbornadienyl cation approaches twice that of the 7-norbornenyl cation as β_{26}/β_{23} and β_{27}/β_{23} both approach zero.

(10) Compare E. Heilbronner, *Tetrahedron Letters*, 1923 (1964).

(11) S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960); P. R. Story, L. C. Snyder, D. C. Douglas, E. W. Anderson, and R. L. Kornegay, *ibid.*, **85**, 3630 (1963).

(12) R. A. Finnegan and R. S. McNees, *J. Org. Chem.*, **29**, 3234 (1964).

(13) A. S. Kende and T. L. Bogard, *Tetrahedron Letters*, 3383 (1967).

first double bond is the most exothermic of any yet recorded.[14]

Acknowledgment. The author is greatly indebted to R. Hoffmann for many stimulating discussions and to National Science Foundation and Public Health Service Research Grants GP-7479 and 10495-01 (National Cancer Institute) for financial support.

(14) R. B. Turner, *J. Am. Chem. Soc.*, **86**, 3586 (1964).

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On the Radiation-Induced Polymerization of Isobutylene under Anhydrous Conditions and the Effect of Solid Additives[1]

Sir:

There have been persistent claims from several laboratories that the rates of the radiation-induced ionic polymerization of isobutylene can be markedly increased in the presence of certain solid additives.[2] Most of the detailed quantitative work on this subject refers to the use of silica, alumina, and zinc oxide powders with high surface areas.[2] It has been argued that the mechanism of the reaction is essentially heterogeneous, and that the role of the solid is to provide electron traps[2a] or some other ill-defined means of positive-ion stabilization,[2b] thereby acting to extend the ionic chain. In addition, a recent correlation of this enhancement effect with the semiconductor properties of solids has been proposed.[2d]

Because it has been established[3] that low concentrations of water exert a strong retarding effect on the rates of many radiation-induced ionic polymerizations, our interest was inevitably drawn to the above subject[2] by the lingering suspicion[3a] that the reason for the observed effects could be trivial in origin, deriving only from the action of the solid as an efficient dehydrating agent for the liquid monomer. In an attempt to resolve this question unambiguously,[4] isobutylene samples of extreme dryness have been prepared in the present study without bringing the monomer into contact with a dispersed solid adsorbent at any stage, either before or during irradiation. This avoids the possibility of any adventitious carryover of finely divided solid into the irradiation cell.

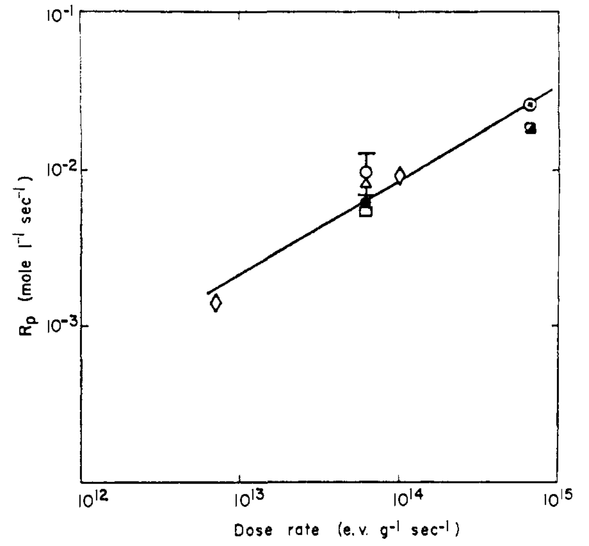

Figure 1. Dose rate dependence of rate of polymerization of isobutylene: ○, mean of nine separate runs at 0° (the horizontal bars represent the average deviation from the mean); ●, mean of two runs at 0° from batch 9; ⊙, mean of two runs at 0° from batch 9; ◪, mean of four runs at −78°; □, mean of four runs at −78°; △, mean of three runs at 27°; ◇, taken from ref 2b at −78 and 0° (see text). The straight line is drawn between the data points marked by ● and ⊙.

Full details of experimental technique will be described elsewhere.[5]

Isobutylene (Phillips Research Grade, 99.59 mole %) was distilled *in vacuo* over refluxing sodium–potassium alloy[6] at 300° in a greaseless apparatus constructed of Pyrex glass and metal valves. The dry monomer was then distilled from a reservoir held at −78° through a breakseal into an all-glass manifold with attached sample tubes which had been previously baked out for up to 150 hr at 500° and 10^{-7} torr by means of an ultrahigh-vacuum pumping installation.

A comparison of our results with those of Dalton[2b] appears in Figure 1. It should be noted that each of the two data points taken from the latter work represents the maximum in the R_p–zinc oxide composition curve at the corresponding dose rate. Moreover, these particular rates are considerably higher than any of the other results, at similar dose rates, in the literature.[2] On the other hand, the points shown from the present work without additive refer to the mean of several runs, and the straight line denotes the dependence of the mean R_p on dose rate I for a set of samples prepared from the same batch of monomer and irradiated at 0°, for which the exponent $\Delta \log R_p/\Delta \log I$ is 0.6. An exponent close to 0.5 is expected[7] under conditions of negligible impurity termination. As observed for the reaction in the presence of zinc oxide,[2b] this study also suggests that the variation of R_p with temperature at constant dose rate is relatively minor between 27 and −78°.

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(1) This work was supported by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-2968. This is AEC Document No. ORO-2968-26.

(2) (a) A review of the extensive earlier work in this field is given by S. H. Pinner, "The Chemistry of Cationic Polymerization," P. H. Plesch, Ed., Pergamon Press Ltd., Oxford, 1963, p 611; (b) F. L. Dalton, *Polymer*, **6**, 1 (1965); J. A. Bartlett and F. L. Dalton, *ibid.*, **7**, 107 (1966); (c) C. David, F. Provoost, and G. Verduyn, *J. Polymer Sci.*, **C1**, 1135 (1963); (d) L. P. Mezhirova, A. D. Abkin, A. I. Popova, L. P. Tolstoukhova, and A. P. Sheinker, Abstract of Paper B21 presented at XXth International Congress of Pure and Applied Chemistry, Moscow, 1965, reproduced in AEC Document No. TID-22360; (e) for the alleged effect of additives on the polymerization rate of other monomers, see, *e.g.*, A. Charlesby and J. Morris, *Proc. Roy. Soc.* (London), **A281**, 392 (1964).

(3) (a) T. H. Bates, J. V. F. Best, and F. Williams, *Nature*, **188**, 469 (1960); *Trans. Faraday Soc.*, **58**, 192 (1962); (b) for a review of more recent work with detailed references, see F. Williams in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., John Wiley and Sons, Inc., New York, N. Y., in press.

(4) *Cf.* E. V. Kristal'nyi and S. S. Medvedev, *Vysokomol. Soedin.*, **7**, 1373, 1377 (1965). These authors concur with the suggestion[3a] that the solid additives serve to remove traces of water. They present evidence showing that after pretreatment with zinc oxide, isobutylene undergoes radiation-induced polymerization at −78° at the same rate as in the presence of zinc oxide. The highest polymerization rates and $G(-m)$ values obtained by these authors are about a factor of 10 lower than the results obtained in the present work under the same conditions of temperature (−78°) and dose rate (*ca.* 3.6×10^4 rads/hr).

(5) R. B. Taylor, M.S. Thesis, University of Tennessee.

(6) We use 78% potassium alloy corresponding to the eutectic composition. This pure liquid alloy is supplied by the MSA Research Corp., Callery, Pa. 16024.

(7) F. Williams, Ka. Hayashi, K. Ueno, Ko. Hayashi, and S. Okamura, *Trans. Faraday Soc.*, **63**, 1501 (1967).