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GROUND STATES OF CONJUGATED MOLECULES—VI

CALICENE DERIVATIVES[1,2]

M. J. S. DEWAR and G. J. GLEICHER
Department of Chemistry, The University of Texas, Austin, Texas, 78712, U.S.A.

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Abstract—Calculations have been carried out for calicene and its various possible benzo derivatives, by the semi-empirical SCF MO procedures described in previous papers.[3,4] The results imply that calicene is not aromatic, showing strong bond fixation and having a negligible resonance energy.

SOME time ago Roberts *et al.*[5] predicted on the basis of Hückel calculations that calicene[6] (I) should be aromatic, its delocalization energy (2·94β) being much greater than that (2β) of benzene. This work has recently attracted attention in view of the synthesis of derivatives of I in several different laboratories.[7]

The Hückel method is, however, a most unreliable guide in the case of such compounds; for example it also predicts a very large delocalization energy (1·5β) for fulvene, a compound known to show no aromatic properties whatsoever. In view of the current interest in this ring system, and at the suggestion of Professor H. Prinzbach, we therefore decided to study calicene and its benzo derivatives using the SCF MO procedure which we have recently devised.[3,4] This method has so far given satisfactory results in all cases where it has been tried; for example it predicts that fulvene should be a "classical" polyene with strong bond fixation and virtually zero resonance energy, a conclusion which seems to be in good agreement with the available experimental evidence.

Table I lists π-binding energies for the various molecules shown in Fig. 1, calculated by four different methods. Two different sets of values were used for the repulsion integrals, one set (PPP) corresponding closely to the values recommended by Pariser and Parr,[8] the other (SPO) to a modified[3,4] split p-orbital treatment; in each case the calculations were carried out first with the assumption that all bonds have a common "aromatic" length (1·40Å), and secondly by an iterative[4] procedure in which allowance is made for variations in the various integrals with bond length. This second procedure provides estimates of bond lengths as well as π-energies; the values calculated in this way are shown in Fig. 1.

Table 1 indicates that the most stable form of these molecules is usually one with significant bond alternation; in particular the "double" bond joining the three- and

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[2] For Part V, see M. J. S. Dewar and G. J. Gleicher, *Tetrahedron* **1**, 1817 (1965).

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[5] J. D. Roberts, A. Streitwieser, and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

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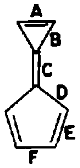
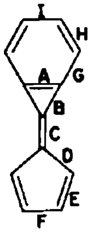
Fig. 1. Bond lengths (Å) in calicene derivatives, estimated by the PPP (SPO) methods.



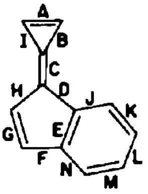
I

A = 1·349 (1·345)
B = 1·469 (1·476)
C = 1·370 (1·361)
D = 1·451 (1·460)
E = 1·361 (1·355)
F = 1·446 (1·455)



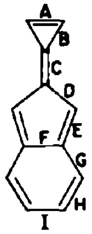
II

A = 1·399 (1·394)
B = 1·471 (1·478)
C = 1·370 (1·361)
D = 1·451 (1·460)
E = 1·361 (1·356)
F = 1·446 (1·455)
G = 1·405 (1·407)
H = 1·390 (1·387)
I = 1·404 (1·407)



III

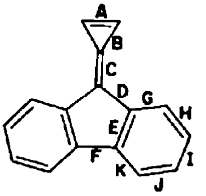
A = 1·349 (1·346)
B = 1·469 (1·476)
C = 1·368 (1·360)
D = 1·456 (1·464)
E = 1·405 (1·406)
F = 1·453 (1·461)
G = 1·359 (1·353)
H = 1·452 (1·462)
I = 1·468 (1·476)
J = 1·407 (1·408)
K = 1·391 (1·389)
L = 1·404 (1·406)
M = 1·390 (1·388)
N = 1·408 (1·409)



IV

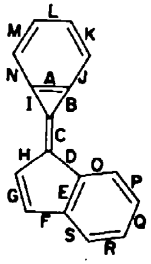
A = 1·349 (1·345)
B = 1·468 (1·476)
C = 1·376 (1·365)
D = 1·444 (1·455)
E = 1·373 (1·364)
F = 1·450 (1·457)
G = 1·454 (1·465)
H = 1·360 (1·353)
I = 1·444 (1·456)

FIG. 1 (*Continued*)



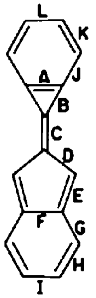
V

A = 1·349 (1·346)
B = 1·469 (1·476)
C = 1·366 (1·359)
D = 1·457 (1·465)
E = 1·406 (1·402)
F = 1·460 (1·465)
G = 1·406 (1·406)
H = 1·392 (1·391)
I = 1·402 (1·403)
J = 1·392 (1·391)
K = 1·404 (1·405)



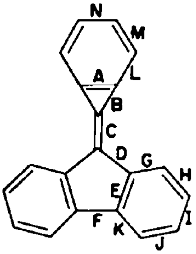
VI

A = 1·402 (1·397)
B = 1·465 (1·472)
C = 1·368 (1·360)
D = 1·459 (1·466)
E = 1·405 (1·400)
F = 1·455 (1·462)
G = 1·357 (1·352)
H = 1·455 (1·465)
I = 1·465 (1·472)
J = 1·405 (1·407)
K = 1·391 (1·388)
L = 1·404 (1·406)
M = 1·391 (1·388)
N = 1·405 (1·407)
O = 1·407 (1·408)
P = 1·391 (1·388)
Q = 1·404 (1·406)
R = 1·390 (1·388)
S = 1·407 (1·408)



VII

A = 1·398 (1·392)
B = 1·472 (1·480)
C = 1·376 (1·366)
D = 1·443 (1·453)
E = 1·374 (1·365)
F = 1·450 (1·456)
G = 1·454 (1·464)
H = 1·360 (1·354)
I = 1·443 (1·455)
J = 1·405 (1·408)
K = 1·390 (1·387)
L = 1·404 (1·407)



VIII

A = 1·401 (1·397)
B = 1·470 (1·476)
C = 1·366 (1·359)
D = 1·458 (1·465)
E = 1·406 (1·402)
F = 1·461 (1·466)
G = 1·405 (1·405)
H = 1·393 (1·392)
I = 1·401 (1·402)
J = 1·393 (1·392)
K = 1·404 (1·404)
L = 1·403 (1·405)
M = 1·392 (1·390)
N = 1·403 (1·405)

TABLE 1. π-BINDING ENERGIES OF THE CALICENES (ev)

Molecule[c]	Fixed β[a]		Variable β[b]	
	PPP	SPO	PPP	SPO
Calicene (I)	9·758	8·877	10·176	9.610
2,3-Benzcalicene (II)	15·843	14·361	15·831	14·663
2′,3′-Benzcalicene (III)	15·771	14·306	16·109	14·877
3′,4′-Benzcalicene (IV)	15·111	13·634	15·375	14·454
2′,3′,4′,5′-Dibenzcalicene (V)	21·860	19·798	21·983	20·096
2,3,2′,3′-Dibenzcalicene (VI)	21·877	19·800	21·796	19·914
2,3,3′,4′-Dibenzcalicene (VII)	21·175	19·108	21·054	19·513
Tribenzcalicene (VIII)	27·979	25·296	27·606	25·125

[a] Based on bond lengths of 1·40Å.
[b] Allowing for variations in bond lengths.
[c] Structures given in Fig. 1.

five-membered rings is predicted to be short (1·37Å), while the adjacent "single" bonds are long (1·45–1·48Å). These values do not of course allow for possible shortening of the bonds in the three-membered ring, due to the fact that their σ-components are "bent"; analogy with cyclopropane suggests that this effect could shorten them by ca. 0·02Å.

It was shown in Part III[4] that the calculated heats of formation of classical polyenes[9] can be expressed as additive functions of C—C and C═C bond energies; on this basis such polyenes can be regarded as having localized single and double bonds. The resonance energy of a hydrocarbon can then be defined as the difference between its heat of formation, and the heat of formation calculated for a single classical structure by using those empirical bond energies. Table 2 lists resonance energies calculated in this way for compounds I–VIII; the heats of formation were estimated in the manner indicated in previous papers[4] of this series, using the π-binding energies calculated for the bond lengths indicated in Fig. 1.

These results suggest, in direct contradiction to the results of the Hückel calculations,[5] that calicene (I) is *not* an aromatic system. Our estimate for the resonance

TABLE 2. RESONANCE ENERGIES OF THE CALICENES (ev)

Molecule[a]	E_R	
	PPP	SPO
Calicene (I)	0·064	0·093
2,3-Benzcalicene (II)	1·304	1·400
2′,3′-Benzcalicene (III)	1·582	1·614
3′,4′-Benzcalicene (IV)	0·039	0·072
2′,3′,4′,5′-Dibenzcalicene (V)	3·042	3·087
2,3,2′,3′-Dibenzcalicene (VI)	2·855	2·905
2,3,3′,4′-Dibenzcalicene (VII)	1·303	1·385
Tribenzcalicene (VIII)	4·250	4·370

[a] Structures given in Fig. 1.

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[9] A classical polyene is one for which only a single classical (unexcited) resonance structure can be written.

energy of I is very small (1·5 kcal/mole) and the bond lengths show strong alternation. Even more striking are the results for 3′,4′-benzocalicene (IV); this also is predicted to have a negligible resonance energy (0·9 kcal/mole), implying that the fixation of bonds in the calicene system is sufficient to destroy the aromaticity of the six-membered ring. The remaining compounds are benzo derivatives of I or IV; their resonance energies have values close to what one would predict for a corresponding number of benzene rings, assuming I and IV to be classical polyenes with virtually fixed bonds.