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GROUND STATES OF CONJUGATED MOLECULES—V

FUSED CYCLOBUTADIENES[1]

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Abstract—Resonance energies have been calculated for a number of polycyclic aromatic hydrocarbons containing a cyclobutadiene ring, using the SCF MO method developed in previous papers of this series.[2] The calculated values seem to correlate well with the properties reported for these compounds. The calculated heat of formation of biphenylene leads to a new value for the strain energy.

INTRODUCTION

THE properties of cyclobutadiene and its derivatives play a crucial role in theories of aromaticity; much experimental and theoretical work on this problem has been reported in recent years.

Cyclobutadiene has never been prepared in the free state; attempts to isolate it, or simple derivatives of it, under mild conditions have invariably led to dimers.[3] On the other hand dibenzocyclobutadiene (biphenylene) has been known for some time[4] and a number of analogous polycylic hydrocarbons have been prepared in the last decade, notably by Cava and his associates.[5] These differ greatly in stability, depending on the nature of the two aromatic residues fused to the cyclobutadiene ring.

Numerous attempts have been reported[3] to prepare analogous compounds containing only one residue fused to butadiene; in all cases dimers were obtained, indicating that such compounds, like cyclobutadiene itself, are too reactive to be isolated. Recently, however, Cava has been able to prepare monomeric 1,2-diphenylnaphtho[b]cyclobutadiene (XIII); apparently the two phenyl substituents are sufficient to stabilize the naphthocyclobutadiene system.

Attempts have been made to explain these observations theoretically, in terms of calculations based on the simple Hückel MO method;[6] however the Hückel method gives reliable results only for aromatic hydrocarbons[7]—and the evidence suggests that cyclobutadiene is not an aromatic system. The Hückel method fails for hydrocarbons when the bonds are unequal in length, and in the case of the annulenes it fails to account for the success of Hückel's rule.[2]

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[1] This work was supported by the National Institutes of Health, U.S. Public Health Service, through Grant Number GM 11531-01.

[2a] A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.* **42**, 756 (1965).

[b] M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.* **87**, 685 (1965).

[c] *Ibid.* **87**, 692 (1965).

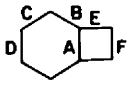
[3] cf. R. Criegee and G. Schröder, *Leibig's Ann.* **623**, 1 (1959); H. H. Freedman, *J. Amer. Chem. Soc.* **83**, 2195 (1961).

[4] W. C. Lothrop, *J. Amer. Chem. Soc.* **63**, 1187 (1941).

[5] See M. P. Cava, B. Huang, and J. Van Meter, *J. Amer. Chem. Soc.* **85**, 4032 (1963) and Ref cited there.

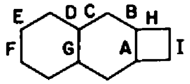
[6] See M. Asgar Ali and C. A. Coulson, *Tetrahedron* **10**, 41 (1960); C. A. Coulson and M. D. Poole, *Ibid.* **20**, 1859 (1964).

[7] See M. J. S. Dewar, *Rev. Mod. Phys.* **35**, 586 (1963).



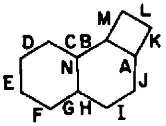
I

A = 1·417 (1·423)
B = 1·381 (1·376)
C = 1·416 (1·421)
D = 1·381 (1·377)
E = 1·485 (1·487)
F = 1·348 (1·347)



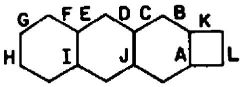
II

A = 1·440 (1·447)
B = 1·367 (1·362)
C = 1·440 (1·447)
D = 1·413 (1·415)
E = 1·386 (1·383)
F = 1·409 (1·412)
G = 1·404 (1·399)
H = 1·477 (1·480)
I = 1·351 (1·349)



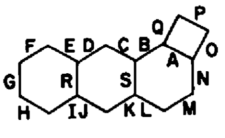
III

A = 1·394 (1·392)
B = 1·408 (1·407)
C = 1·432 (1·439)
D = 1·372 (1·367)
E = 1·426 (1·435)
F = 1·373 (1·367)
G = 1·432 (1·439)
H = 1·409 (1·408)
I = 1·393 (1·392)
J = 1·401 (1·403)
K = 1·493 (1·495)
L = 1·346 (1·345)
M = 1·491 (1·494)
N = 1·415 (1·409)



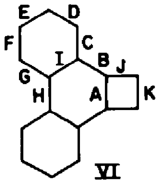
IV

A = 1·448 (1·456)
B = 1·364 (1·359)
C = 1·447 (1·455)
D = 1·391 (1·387)
E = 1·414 (1·417)
F = 1·428 (1·433)
G = 1·375 (1·371)
H = 1·422 (1·429)
I = 1·412 (1·406)
J = 1·421 (1·422)
K = 1·474 (1·477)
L = 1·352 (1·350)



V

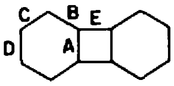
A = 1·384 (1·379)
B = 1·420 (1·424)
C = 1·413 (1·416)
D = 1·396 (1·390)
E = 1·438 (1·446)
F = 1·369 (1·363)
G = 1·431 (1·441)
H = 1·369 (1·363)
I = 1·437 (1·446)
J = 1·396 (1·391)
K = 1·412 (1·415)
L = 1·421 (1·425)
M = 1·383 (1·379)
N = 1·411 (1·418)
O = 1·495 (1·498)
P = 1·346 (1·345)
Q = 1·494 (1·496)
R = 1·423 (1·423)
S = 1·420 (1·414)



VI

A = 1·373 (1·368)
B = 1·430 (1·436)
C = 1·420 (1·423)
D = 1·381 (1·377)
E = 1·415 (1·420)
F = 1·382 (1·378)
G = 1·418 (1·422)
H = 1·436 (1·440)
I = 1·406 (1·399)
J = 1·497 (1·499)
K = 1·345 (1·344)

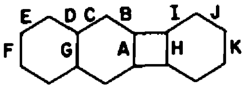
Fig. 1. Structures of hydrocarbons discussed in this paper, together with bond lengths calculated by the PPP (SPO) methods.



VII

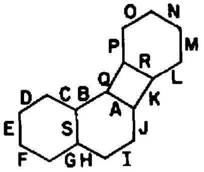
A = 1·411 (1·413)
B = 1·389 (1·385)
C = 1·407 (1·410)
D = 1·389 (1·386)
E = 1·478 (1·481)

experimental values[8]
A = 1·38
B = 1·38
C = 1·42
D = 1·36
E = 1·52



VIII

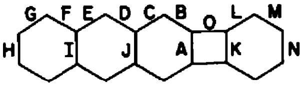
A = 1·433 (1·440)
B = 1·372 (1·367)
C = 1·433 (1·440)
D = 1·418 (1·421)
E = 1·382 (1·378)
F = 1·413 (1·418)
G = 1·405 (1·398)
H = 1·408 (1·410)
I = 1·392 (1·390)
J = 1·404 (1·406)
K = 1·391 (1·389)
L = 1·474 (1·477)



IX

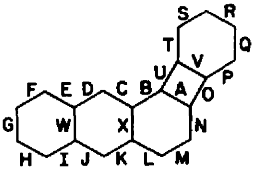
A = 1·390 (1·385)
B = 1·417 (1·419)
C = 1·428 (1·434)
D = 1·375 (1·370)
E = 1·422 (1·429)
F = 1·375 (1·370)
G = 1·427 (1·433)
H = 1·417 (1·419)
I = 1·385 (1·382)
J = 1·410 (1·414)
K = 1·482 (1·486)

L = 1·386 (1·382)
M = 1·410 (1·414)
N = 1·386 (1·383)
O = 1·410 (1·414)
P = 1·386 (1·383)
Q = 1·480 (1·484)
R = 1·413 (1·416)
S = 1·410 (1·404)



X

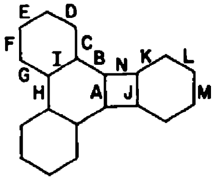
A = 1·442 (1·450)
B = 1·368 (1·362)
C = 1·442 (1·450)
D = 1·396 (1·393)
E = 1·409 (1·411)
F = 1·431 (1·437)
G = 1·374 (1·368)
H = 1·425 (1·432)
I = 1·414 (1·409)
J = 1·419 (1·418)
K = 1·406 (1·408)
L = 1·394 (1·392)
M = 1·402 (1·404)
N = 1·393 (1·391)
O = 1·472 (1·475)



XI

A = 1·381 (1·375)
B = 1·428 (1·434)
C = 1·407 (1·408)
D = 1·400 (1·397)
E = 1·435 (1·443)
F = 1·371 (1·365)
G = 1·429 (1·438)
H = 1·371 (1·364)
I = 1·435 (1·443)
J = 1·400 (1·397)
K = 1·407 (1·407)
L = 1·428 (1·434)
M = 1·377 (1·371)
N = 1·420 (1·428)

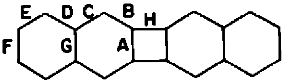
O = 1·483 (1·486)
P = 1·385 (1·381)
Q = 1·411 (1·415)
R = 1·385 (1·382)
S = 1·411 (1·415)
T = 1·386 (1·382)
U = 1·481 (1·485)
V = 1·414 (1·417)
W = 1·420 (1·418)
X = 1·419 (1·414)



XII

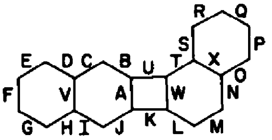
A = 1·374 (1·368)
B = 1·435 (1·441)
C = 1·416 (1·419)
D = 1·383 (1·380)
E = 1·412 (1·416)
F = 1·384 (1·380)
G = 1·415 (1·418)
H = 1·440 (1·445)
I = 1·405 (1·399)
J = 1·415 (1·417)
K = 1·384 (1·380)
L = 1·412 (1·417)
M = 1·384 (1·380)
N = 1·483 (1·485)

FIG. 1 (*Continued*).



XIII

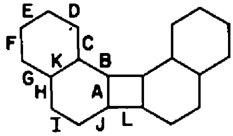
A = 1·431 (1·437)
B = 1·375 (1·370)
C = 1·431 (1·436)
D = 1·419 (1·423)
E = 1·381 (1·377)
F = 1·415 (1·419)
G = 1·406 (1·399)
H = 1·471 (1·474)



XIV

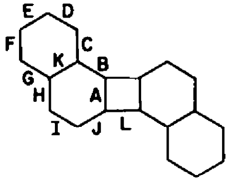
A = 1·436 (1·442)
B = 1·371 (1·366)
C = 1·436 (1·442)
D = 1·416 (1·419)
E = 1·383 (1·380)
F = 1·412 (1·416)
G = 1·383 (1·380)
H = 1·416 (1·419)
I = 1·436 (1·442)
J = 1·370 (1·365)
K = 1·476 (1·479)
L = 1·414 (1·418)
M = 1·383 (1·379)

N = 1·420 (1·423)
O = 1·426 (1·431)
P = 1·377 (1·372)
Q = 1·421 (1·428)
R = 1·376 (1·372)
S = 1·426 (1·431)
T = 1·419 (1·423)
U = 1·474 (1·478)
V = 1·405 (1·398)
W = 1·489 (1·384)
X = 1·409 (1·403)



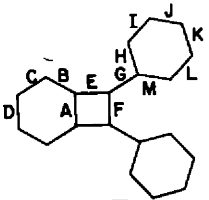
XV

A = 1·390 (1·387)
B = 1·414 (1·413)
C = 1·429 (1·435)
D = 1·374 (1·369)
E = 1·423 (1·431)
F = 1·375 (1·369)
G = 1·429 (1·435)
H = 1·414 (1·416)
I = 1·388 (1·385)
J = 1·407 (1·411)
K = 1·412 (1·406)
L = 1·484 (1·490)



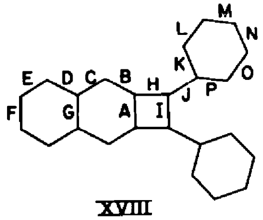
XVI

A = 1·390 (1·387)
B = 1·414 (1·415)
C = 1·429 (1·435)
D = 1·375 (1·369)
E = 1·423 (1·431)
F = 1·375 (1·369)
G = 1·429 (1·434)
H = 1·415 (1·416)
I = 1·387 (1·384)
J — 1·408 (1·411)
K = 1·412 (1·406)
L = 1·485 (1·489)



XVII

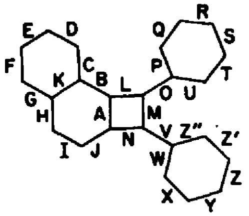
A = 1·416 (1·421)
B = 1·383 (1·378)
C = 1·414 (1·419)
D = 1·382 (1·379)
E = 1·484 (1·486)
F = 1·362 (1·357)
G = 1·457 (1·464)
H = 1·403 (1·402)
I = 1·395 (1·395)
J = 1·398 (1·398)
K = 1·397 (1·397)
L = 1·397 (1·397)
M = 1·401 (1·400)



XVIII

A = 1·439 (1·446)
B = 1·368 (1·363)
C = 1·439 (1·446)
D = 1·414 (1·416)
E = 1·385 (1·383)
F = 1·410 (1·413)
G = 1·404 (1·398)
H = 1·476 (1·479)
I = 1·364 (1·359)
J = 1·457 (1·464)
K = 1·403 (1·401)
L = 1·395 (1·395)
M = 1·398 (1·398)
N = 1·397 (1·397)
O = 1·397 (1·397)
P = 1·401 (1·400)

Fig. 1 (*Continued*).



XIX

A = 1·392 (1·390)
B = 1·410 (1·410)
C = 1·431 (1·438)
D = 1·373 (1·368)
E = 1·425 (1·433)
F = 1·373 (1·368)
G = 1·431 (1·438)
H = 1·411 (1·411)
I = 1·391 (1·389)
J = 1·403 (1·405)
K = 1·414 (1·408)
L = 1·489 (1·492)
M = 1·360 (1·355)
N = 1·491 (1·494)

O = 1·457 (1·464)
P = 1·403 (1·402)
Q = 1·395 (1·395)
R = 1·399 (1·399)
S = 1·397 (1·397)
T = 1·397 (1·397)
U = 1·401 (1·400)
V = 1·456 (1·464)
W = 1·403 (1·402)
X = 1·395 (1·395)
Y = 1·399 (1·399)
Z = 1·397 (1·397)
Z′ = 1·397 (1·397)
Z″ = 1·402 (1·400)

FIG. 1 (*Continued*).

We have recently developed variants of the Pople SCF MO method which seem to provide good estimates for heats of formation and resonance energies of conjugated hydrocarbons, regardless of whether they are aromatic, non-aromatic, or antiaromatic; here we wish to report the results of some calculations of this kind for compounds containing the cyclobutadiene system.

THEORETICAL METHOD

Our procedure[2] is a variant of the Pople SCF MO method in which refinements have been introduced; (a) the one-electron resonance integrals (β) are estimated from a thermochemical rather than spectral data; (b) the core repulsion is calculated using a better core potential; (c) modifications are made in the electron repulsion integrals; a set similar to those recommended by Pariser and Parr ("PPP" values below), and a set corresponding to an intermediate SPO approximation ("SPO" values below). Calculations were also carried out (a) assuming all C—C bonds to have a common "aromatic" length, 140 Å, and (b) by a self-consistent procedure which calculates changes in bond lengths by assuming a relation between bond length and bond order. Full details of the procedure will be found in Part II.[2b] The calculations were carried out using the CDC 1604 computer at the Computation Centre here.

RESULTS AND DISCUSSION

Calculations were carried out for the compounds listed in Fig. 1. Table 1 lists total π-bond energies ($E_{\pi b}$), and resonance energies (E_R), calculated assuming *equal* bond lengths throughout; in this case it is easily shown[2b] that:

$$E_R = N_{CC}\left[A_0 + \frac{N' - N''}{2N_{CC}}(E'' - E')\right] + E_{\pi b} \qquad (1)$$

where N', N'' are respectively the numbers of single and double carbon-carbon bonds in a single classical structure, the corresponding bond energies being E', E''; N_{CC} is

TABLE 1. π-BINDING AND RESONANCE (ev) FOR SOME CYCLOBUTADIENES[a]

		PPP			SPO	
Molecule	$E_{\pi b}$	E_R	E_R'	$E_{\pi b}$	E_R	E_R'
I	9·837	0·830	−0·488	9·058	1·046	−0·172
II	15·635	1·968	−0·314	14·263	2·145	−0·135
III	15·334	1·667	−0·615	14·008	1·890	−0·390
IV	21·169	2·843	−0·243	19·227	3·003	−0·075
V	20·756	2·430	−0·656	18·867	2·643	−0·435
VI	21·065	2·739	−0·716	19·191	2·967	−0·467
VII	16·277	2·610	−0·026	17·797	2·579	−0·057
VIII	21·997	3·671	+0·071	19·943	3·719	+0·121
IX	21·841	3·515	−0·085	19·802	3·578	−0·020
X	27·501	4·516	+0·112	24·882	4·552	+0·156
XI	27·287	4·302	−0·102	24·680	4·350	−0·046
XII	27·622	4·637	−0·140	25·017	4·687	−0·065
XIII	27·692	4·707	+0·143	25·066	4·736	+0·176
XIV	27·587	4·602	+0·038	24·972	4·642	+0·082
XV	27·385	4·401	−0·163	24·787	4·457	−0·103
XVI	27·384	4·400	−0·164	24·786	4·456	−0·104
XVII	26·704	4·028	−0·191	24·298	4·168	−0·099
XVIII	32·490	5·156	−0·027	29·498	5·261	+0·032
XIX	32·215	4·881	−0·302	29·256	5·019	−0·110

[a] All bond lengths equal 1·40 Å.

the total number of carbon-carbon bonds (i.e. $N_{CC} = N' + N''$); A_0 is a constant determined from data for benzene and having the values −1·0871 ev (for PPP calculations), or −0·9765 ev (for SPO calculations).

The fourth and seventh columns of Table 1 show differences (E_R') in resonance energy between the various cyclobutadiene derivatives, and the pair of π-systems obtained by breaking the two bonds represented by horizontal lines in each formula in Fig. 1. Thus E_R' for biphenylene (VII) is the difference in resonance energy between VII and two molecules of benzene, the negative value implying that the latter have the higher resonance energy. Thus a positive value of E_R' implies that the corresponding cyclobutadiene ring is aromatic, a negative value that it is antiaromatic; compounds with large negative values of E_R' should then be chemically unstable, tending to undergo reactions which destroy the unfavorable effect of conjugation in the antiaromatic four-membered ring. In calculating E_R', we used for the various component aromatic systems the values of E_R listed in Table 2.

The values of E_R' in Table 1 seem to account well for the observed behavior of these compounds. Thus all attempts to make I, II or III have failed, only dimers being isolated; all these compounds have large negative values of E_R' and so should tend to dimerize easily. On the other hand the corresponding diphenyl derivatives (XVII, XVIII and XIX) have values of E_R' which, while still negative, are numerically less than for the unsubstituted compounds, that for XVIII being close to zero (PPP) or positive (SPO); recently XVIII has been isolated as a stable monomer.

The compounds with two aryl systems fused to the four-membered ring mostly have values for E_R' that are positive, or close to zero; of these VII, VIII, IX, XIII, XV and perhaps XVI are known. None of the other compounds of this type in Fig. 1 has as yet been reported—but this may be because no one has tried to make them;

TABLE 2. RESONANCE ENERGIES OF REFERENCE MOLECULES[a]

	E_R	
Molecule	PPP	SPO
Benzene	1·318	1·318
Naphthalene	2·282	2·280
Anthracene	3·086	2·078
Phenanthrene	3·455	3·434
cis-Stilbene	2·901	2·949

[a] Bond lengths equal to 1·40 Å.

our calculations suggest that these should all be stable, their E_R' being more positive than that for the known XV.

Qualitative chemical evidence suggests that VIII is more stable than IX, and XIII than XV; this again correlates well with our calculations, the more stable isomer having in each case the larger value for E_R'. It is unfortunate that no thermochemical data are available for these compounds, other than VII, to test our quantitative predictions of resonance energies; while strain effects would make it difficult to compare the calculated and observed values for any one compound, they should not affect the relative values for different members of the series; for the strain energies should be much the same in each.

TABLE 3. BINDING ENERGIES (ev) OF SOME CYCLOBUTADIENES[a]

	$E_{\pi b}$	
Molecule	PPP	SPO
I	10·256	9·563
II	15·944	14·745
III	15·665	14·479
IV	21·389	19·729
V	20·973	19·324
VI	21·308	19·609
VII	16·262	14·853
VIII	21·903	20·015
IX	21·743	19·869
X	27·322	24·970
XI	27·084	24·754
XII	27·419	25·021
XIII	27·514	25·155
XIV	27·414	25·064
XV	27·188	24·828
XVI	27·188	24·830
XVII	26·816	24·575
XVIII	32·505	29·765
XIX	32·231	29·500

[a] Bonds allowed to assume self-consistent length.

We have also carried out calculations by the alternative[2b] procedure in which allowance is made for changes in bond length. Table 3 lists calculated total π-bond energies ($E_{\pi b}$) for the nineteen hydrocarbons. In this case resonance energies cannot be calculated by the methods used for other aromatic systems in Part II;[2b] for the bond lengths in the cyclobutadiene derivatives vary widely and the mean bond lengths for the compounds in Table 1 also differ significantly for the "normal" aromatic value, 1·40 Å. In order to calculate accurate resonance energies it would be necessary to allow explicitly for the variations in compression energy of the σ-bonds with bond length; this we have not yet done. However the results in the preceding paper suggest that the resonance energies calculated with fixed bond lengths are usually close to the truth, so that the values for E_R and E_R' in Table 1 are probably reliable.

TABLE 4. HEATS OF FORMATION OF BIPHENYLENE (kcal/mole)

PPP (fixed bond length)	2427·9
SPO (fixed bond length)	2430·0
PPP (variable bond length)	2425·0
SPO (variable bond length)	2423·0
Average	2426·5. ± 2·5
From Heat of Combustion	2399·0 ± 5·0

Fig. 1 shows bond lengths calculated by the self-consistent PPP and SPO treatments,[2b] assuming the relation between bond order (p) and bond length (r) to be:

$$r = (1{\cdot}504 - 0{\cdot}166p)\ \text{Å} \tag{2}$$

Unfortunately there are no reliable experimental values to compare with these, other

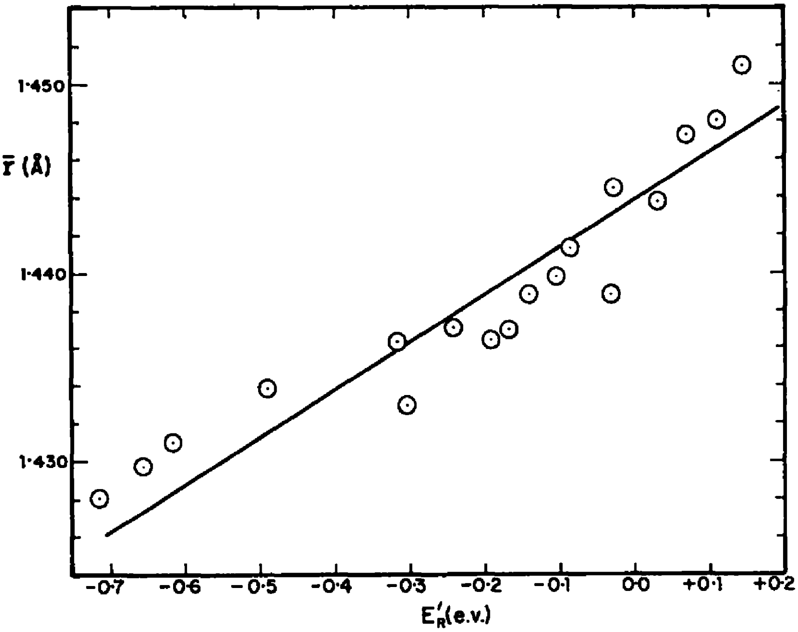


FIG. 2. Plot of E_R' (PPP) vs. $\bar{r}$ for compounds I–XIX.

than a recent structure determination for biphenylene (VII);[8] The reported bond lengths show a general trend similar to that calculated but the quantitative agreement is poor. However it is difficult to assess this since only a preliminary report has as

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[8] T. C. W. Mark and J. Trotter, *Proc. Chem. Soc.* 163 (1961).

yet appeared and in this no limits of error were stated. Moreover the bond lengths differed greatly from those reported in two earlier investigations.[9]

Previous workers have interpreted the stability of these cyclobutadienoid systems in terms of resonance theory on the assumption that the stability should be greater, the greater the contribution of structures in which the bonds in the four-membered ring are single rather than double. While this purely intuitive argument cannot be taken very seriously, we thought it might be amusing to see if our calculated bond lengths showed such a correlation. Fig. 2 shows a plot of the PPP values for E_R' against $\bar{r}$, the calculated mean length of the four bonds in the cyclobutadienoid ring; it will be seen that a correlation does exist, though the points show much scatter.

Since thermochemical data are available for biphenylene[10] we have calculated its heat of formation by the four procedures indicated above (PPP and SPO, fixed and variable bond lengths); the results are shown in Table 4, together with the value calculated from the observed heat of combustion.[10] The four theoretical values agree closely; their mean differs from the experimental value by 27·5 kcal/mole. Since our procedures have proved successful for calculating heats of formation of a wide variety of hydrocarbons, it seems reasonable to equate this difference to the strain energy in VII.

Previous estimates of the strain energy have been much greater than this; thus Coulson and Moffitt[11] calculated it to be 74 kcal/mole, while Springall *et al.*[10] arrived at a value of 57 kcal/mole by comparing the heats of formation of biphenyl and biphenylene and assuming their resonance energies to be the same.

However we feel our value is probably closer to the truth. It is closer to the value (26·2 kcal/mole) for cyclobutane,[12] a compound with less angle strain than VII, but with more conformational strain (due to bond eclipsing).

[9] J. Waser and V. Schomaker, *J. Amer. Chem. Soc.* **65**, 1451 (1943); J. Waser and C.-S. Lu, *Ibid.* **66**, 2035 (1944).

[10] The heat of combustion of VII is 1481 kcal/mole; R. C. Cass, H. D. Springall, and P. G. Quincey, *J. Chem. Soc.* 1188 (1955).

[11] C. A. Coulson and Moffitt, *Phil. Mag.* **40**, 26 (1949).

[12] S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.* **71**, 261 (1952).