products dominate.[6,7,8a,9] All three metal ions react with cyclobutane to produce products in which the ring has been cleaved. Hence, a mechanism involving initial insertion into a C–C bond is postulated (Scheme II). Dehydrogenation products for reactions with cyclopentane and cyclohexane generate complexes that have retained the integrity of the ring. A mechanism involving initial oxidative addition across a C–H bond may be involved; however, this seems unlikely. An alternative mechanism is presented in Scheme VI and involves initial insertion into a C–C bond followed by α-hydride abstraction with concurrent regeneration of the ring. This mechanism requires α-hydride abstraction to be more facile than β-hydride abstraction for metallacyclohexanes and metallacycloheptanes. Ring-cleavage products are also observed for reactions of Co^+ and Ni^+ with cyclopentane and cyclohexane and are proposed to proceed by initial insertion into a C–C bond followed by reversible β-hydride shifts generating a primary alkene–metal ion complex which decomposes according to Scheme IX. Dehydrogenation of deuterated metallacyclopentanes supports this decomposition mechanism.

Several rapid secondary reactions are also observed. A particularly interesting reaction is seen for (ethene)metal(+) which reacts readily with cyclobutane to generate a bis(ethene)–metal ion complex. (Alkene)metal(+) complexes are unreactive with aliphatic alkanes.[29] The bis(ethene)–metal ion complexes are not in equilibrium with metallacyclopentanes as observed in several solution-phase studies.[27] In addition, both Fe^+– and Co^+–cycloalkadiene products react readily with their corresponding cyclic alkanes via multiple dehydrogenations. Similar behavior has been observed for reactions of Fe^+– and Co^+–alkadiene complexes with aliphatic alkanes.[29] In a related study, (cyclopentadienyl)nickel(+) reacts with cyclic alkanes via dehydrogenations.[14] Six sequential H/D exchanges were observed for both $Co\text{-}c\text{-}C_5H_6^+$ and $Fe\text{-}c\text{-}C_5H_6^+$ species with D_2. Reactions of the monodeuterated $M\text{-}c\text{-}C_5H_5D^+$ ions with cyclopentane indicated that the hydrido–cyclopentadienyl complex, **20**, is the reactive species for Fe^+ while the cyclopentadiene species is the reactive form for Co^+.

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Registry No. Fe^+, 14067-02-8; Co^+, 16610-75-6; Ni^+, 14903-34-5; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclopentene, 142-29-0; cyclohexane, 110-82-7; cyclohexene, 110-83-8; methylcyclohexane, 108-87-2.

Ab Initio Calculation of Resonance Energies. Benzene and Cyclobutadiene

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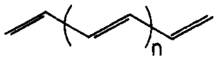
Abstract: Optimum geometries and energies of the all-trans linear polyenes butadiene and hexatriene are obtained with a 6-31G* basis and those of butadiene to pentadecaene in a 3-21G basis. As in semiempirical methods, the energy is a very nearly linear function of chain length. This allows the construction of a Dewar-type aromaticity reference and the computation of ab initio resonance energies for benzene and cyclobutadiene.

It had become apparent by the 1950's that there is very little correlation of the observed stability and chemical behavior of cyclic conjugated systems with Hückel delocalization energy (DE). As more sophisticated theoretical techniques became available, they were also used to compute DE, although with little improvement over the Hückel results. However, in 1969 Dewar and de Llano published resonance energies calculated by the Pariser–Parr–Pople (PPP) method that gave a significant improvement in agreement between theory and experiment.[1] At first sight this success appears to be due to the improved method of computing π energy, but the authors also made a second and more significant change. The Hückel DE of a conjugated hydrocarbon with a Kekulé structure containing n double bonds is defined as the difference between the π energy of the molecule and that of n ethylene units. Dewar and de Llano replaced this ethylene reference by another.

Their new reference structure was based on an earlier observation by Dewar and Gleicher that the acyclic linear polyenes (**1**) are additive in energy.[2] That is, a plot of the calculated π energies of the series **1** vs. n gives an extremely good straight line. This is equivalent to saying that in a linear polyene with $(n + 1)$ single bonds and $(n + 2)$ double bonds, single and double bond energy terms E^π_{C-C} and $E^\pi_{C=C}$ can be determined such that the π energy of the polyene is accurately given by


1

$$E_\pi \approx (n + 1)E^\pi_{C-C} + (n + 2)E^\pi_{C=C} \tag{1}$$

Dewar and de Llano demonstrated that in the PPP approximation a similar additivity also holds for all acyclic conjugated polyenes. On the other hand, for a cyclic molecule this bond energy sum does not always approximate the actual π energy. The bond energy sum is defined as the reference energy, and the difference between this reference energy and the actual energy of the cyclic system is defined as resonance energy (RE). It represents the additional (aromatic), lack of (nonaromatic), or decreased (antiaromatic) stability of the particular cyclic system relative to the additive reference structure. For example, the RE of benzene is the difference between the computed energy of benzene and that of the reference structure which can be thought of as the hypothetical molecule cyclohexatriene (eq 2). Note that the reference

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(1) Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789.

(2) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 685, 692.

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RE = E() − E() (2)

structure contains contributions to its π energy not only from double but also from single bonds (eq 3).

E() $= 3E^{\pi}_{C=C} + 3E^{\pi}_{C-C}$ (3)

We subsequently showed that adaptation of this new reference structure to the Hückel method leads to the computation of resonance energies which agreed equally well, if not better, with experiment for a wide range of conjugated hydrocarbons[3-15] and heterocycles. This indicated that the success of Dewar and de Llano's results was due not to the more sophisticated method of computation (PPP) as they claimed but rather to their definition of a new reference structure.

In principle, it is possible to measure these resonance energies experimentally even though the reference structures are hypothetical. First, if one had available heats of formation for a wide range of acyclic conjugated systems, one could test the predicted additivity of these, and then with heats of formation for cyclic systems, one could obtain experimental resonance energies for comparison with theory. However, these heats of formation are not available, and the energy additivity of the conjugated acyclic hydrocarbons remains untested by experiment. A related question is whether the σ structure of the conjugated systems has been properly accounted for in the two computational methods.[2,3] Dewar and de Llano included the σ energy in a relatively simple empirical way. We showed that the same can be done in the Hückel method, but that, since σ contributions to RE are proportional to π contributions, both can be accounted for by proper parameterization of the Hückel calculation.[16] Thus, depending on the parameters, eq 2 can be used to give either total resonance energy or its π component. Heats of formation were computed to check this treatment of the σ energy. Although they did agree well with experiment, relatively few data were available, and they were for compounds that were quite similar in structure (principally benzenoids). One caution is especially appropriate to cyclobutadiene, however. The linear relation between σ and π energy changes holds most accurately for bonds with π bond orders between 0.3 and 0.9[16] so that some deviation might be expected for the long bonds of cyclobutadiene.

In the absence of sufficient experimental data to answer the questions raised above, one has the alternative of carrying out all-electron calculations (ab initio) on conjugated hydrocarbons. Haddon has in part done this using a minimal basis set with partial geometry optimization of the structures he considered.[17,18] Efficient programs now available[19] allow this problem to be treated at the double-ζ level with complete geometry optimization. Since many of the necessary comparisons involve relatively small differences in large total energies, it is desirable to examine the problem at this higher level though some of our results will do no more than confirm and refine Haddon's previous conclusions. We consider here first the question of additivity in the linear acyclic polyenes (**1**) and second the computation of ab initio resonance energies of benzene and cyclobutadiene.

Table I. Energies (au)

molecule	basis 3-21G	6-31G*
ethylene	−77.600 958	−78.031 719
1,3-butadiene	−154.059 459	−154.919 658
1,3,5-hexatriene	−230.518 801	−231.808 278
1,3,5,7-octatetraene	−306.978 409	
1,3,5,7,9-decapentaene	−383.438 086	
cyclobutadiene	−152.771 514	−153.641 117
benzene	−229.419 451	−230.703 141

Computational Methods

Calculations were performed on the first four linear polyenes, butadiene, hexatriene, octatetraene, and decapentaene, with Pople's 3-21G basis set.[20] All were assumed to be in a planar all-trans geometry (C_{2h} symmetry), but otherwise structures were completely optimized. Haddon and Starnes in their STO-3G calculations on the first three members of this series[17] also assumed planar all-trans geometries in addition to fixing bond angles and C–H lengths. An all-trans structure is consistent with what is known about these polyenes. The fairly common notation using *c* and *t* or *C* and *T* to indicate cis and trans disposition about single or double bonds, respectively, will be convenient in discussing these data. In the case of butadiene, experiment and a previous 4-31G calculation[21,22] agree that the *t* conformation is lower in energy than the *c*. For hexatriene both the *tTt* and *tCt* conformers are stable enough to study by electron diffraction.[23] Commercial samples of hexatriene are reported to contain 60–90% of the *T* conformer,[24,25] and from the heats of hydrogenation in acetic acid solution at 25 °C, Doering[26] found the *T* conformer to be 1.1 kcal/mol more stable than the *C*. A MINDO/2 calculation by Komornicki and McIver[27] agrees with this result in finding the *tTt* conformer to be more stable by 1.5 kcal/mol than the *tCt*. Rotation out of the plane about the single bond lowers the energy of the latter to within 0.8 kcal/mol of the former. Kertêsz, Koller, and Ažman[28] have published STO-3G and 4-31G studies of the *tTt*, *tCt*, and *cTc* conformations, though without geometry optimization. The *tTt* structure is of lowest energy and is 5–8 kcal/mol below *tCt* with the *cTc* conformer between these two in energy. Quite recently a MINDO/3 calculation on the *tTt* structure by Yambe and co-workers[29] was found to give good agreement with Traetteberg's electron diffraction geometry.[23] There appear to be neither experimental structural data nor previous calculations of any sophistication for octatetraene. For decapentaene there is a MINDO/3 calculation on the *tTtTtTt* conformer.[29]

All computations were performed with a DEC 10 version of GAUSSIAN 80.[19] Single point calculations of the SCF energy and gradient were first done on a guessed geometry. The GAUSSIAN 80 gradient was then used in conjunction with a set of both diagonal and off-diagonal force constants to obtain a new geometry from the BMAT link of Pulay's TEXAS program.[30] In all cases it was possible to obtain optimized geometries (largest component of the Cartesian gradient < 0.001) in a single step with BMAT.

For the geometry optimization of butadiene, the 4-31G force constants of Brock, Trachtman, and George[22] were employed with BMAT. For the larger polyenes force constants estimated from those of butadiene

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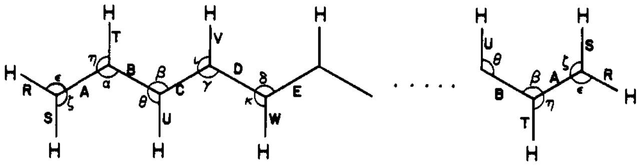
Table II. Optimized Geometries of C_{2h} Linear Polyenes in the 3-21G Basis[a]

	butadiene	hexatriene	octa-tetraene	deca-pentaene
A[b]	1.321 (1.323)	1.322 (1.324)	1.322	1.322
B	1.467 (1.468)	1.462 (1.463)	1.462	1.461
C		1.327 (1.329)	1.328	1.329
D			1.457	1.456
E				1.330
R	1.073 (1.075)	1.072 (1.075)	1.072	1.072
S	1.074 (1.077)	1.074 (1.077)	1.074	1.074
T	1.076 (1.078)	1.076 (1.078)	1.076	1.076
U		1.076 (1.079)	1.076	1.076
V			1.076	1.077
W				1.076
α	123.9 (124.1)	124.1 (124.3)	124.1	124.1
β		124.0 (124.0)	123.9	123.9
γ			124.1	124.1
δ				124.0
ϵ	121.8 (121.7)	121.8 (121.6)	121.8	121.7
ζ	121.8 (121.7)	121.8 (121.8)	121.8	121.8
η	119.9 (119.6)	119.7 (119.4)	119.7	119.7
θ		116.4 (116.5)	116.4	116.5
ι			119.5	119.4
κ				116.5

[a] 6-31G* results are in parentheses. Angles are in degrees and and lengths in angstroms. [b] Labeling of polyene structures:



were used. Optimized geometries and their respective energies were also obtained for butadiene and hexatriene at the 6-31G* level.[31] Even with the efficient GAUSSIAN 80 program each computation of the energy plus gradient for hexatriene required 10 h of DEC 10 CPU time with the 6-31G* basis. It was therefore not possible to use this basis for the larger polyenes. We had previously obtained the optimized geometry and energy of cyclobutadiene in both the 3-21G[32] and 6-31G*[33] bases. Benzene was also computed with these two bases using Pulay's set of force constants[34] in the geometry optimization. Energies are given in Table I, and optimized geometries are summarized in Table II. The optimized geometry of benzene has a C–C bond distance of 1.385 Å and a C–H bond distance of 1.072 Å in the 3-21G basis and 1.386 and 1.075 Å, respectively, in the 6-31G* basis. Cyclobutadiene has an optimized D_{2h} geometry with C–C bond lengths of 1.602 and 1.323 Å, with a C–H length of 1.066 Å and an exterior angle of 134.68° between the C–H and longer C–C bond in the 3-21G basis. The 6-31G* cyclobutadiene geometry is given in ref 33. Orbital energies are shown in Table III. Throughout this work we have used the values of the fundamental constants recommended by Cohen and Taylor;[35] these give 1 hartree = 627.5092 kcal/mol and 1 bohr = 0.529 177 06 Å.

These calculations do not extend to large enough polyenes to contribute much to the question of bond alternation in the infinite chain. In 1939 Coulson[36] observed that Hückel bond orders, and therefore bond lengths, became uniform on moving from the ends toward the interior of an infinite polyene chain. Longuet-Higgins and Salem[37] reexamined the problem, still within the Hückel approximation, and found the equal bond length solution to be an energy maximum instead of a minimum. They predicted bond alternation in the infinite chain. Hückel bond orders can be written in the closed form[38]

$$\rho_{r,r+1} = \{\csc[\pi/(2n+2)] + (-1)^{r-1}\csc[(2r+1)\pi/(2n+2)]\}/(n+1) \quad (4)$$

for the bond between atoms r and $r + 1$ in a polyene of length n. Bond length can then be gotten from bond order by the Coulson-Gołębiewski[39] formula

$$R = 1.517 - 0.180\rho \quad (5)$$

Bond lengths computed by eq 4 and 5 and the 3-21G lengths in Table III both show a tendency toward equalization on going from the end to the center of chains. The same trend is also shown by any adjacent pair of bonds as the chain length is increased. However, these trends are much less pronounced in the 3-21G than in the Hückel results. A plot of the 3-21G bond lengths shows that even if bond equalization were to continue at the same rate in longer chains, it would be necessary to go to a polyene of about 50 carbon atoms before adjacent interior bonds become equal. Thus, from our results it is not possible to predict whether there will be bond alternation or bond equalization in the infinite polyene.

All of this has ignored the question of electron correlation, and the work of Haddon is relevant here. Haddon showed that while the bond alternating structure is slightly more stable than the bond equal structure in SCF calculations on [10]annulene, inclusion of electron correlation reversed the order.[40] However, for [18]annulene[41] the bond alternating structure is 36 kcal/mol below the bond equal structure in an SCF approximation, and it appears doubtful that correlation effects would overcome this larger energy difference. These calculations show that bond alternation occurs fairly early in the [4n + 2]annulene series, though it is somewhat retarded by electron correlation.

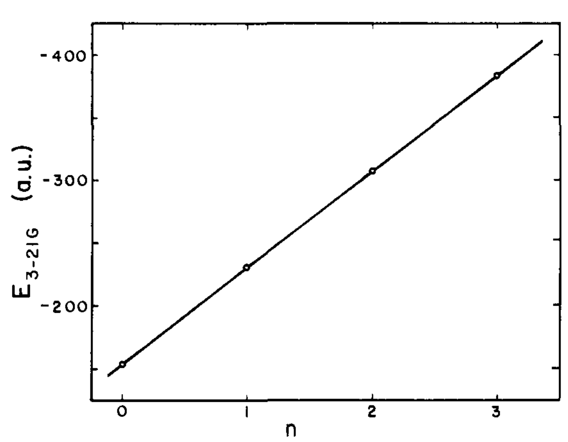


Figure 1. Energy (au) vs. n in the linear polyenes $CH_2{=}CH{-}(CH{=}CH)_n{-}CH{=}CH_2$.

Energy Additivity of Linear Polyenes

As a test of the energy additivity of the linear polyenes, the energies of the first four members of the series are plotted in Figure 1. This additivity is seen to be good; that is, there is a constant increase in energy as n is increased. A better idea of how good the additivity is can be obtained from the first and second energy differences (Table IV). The largest deviation from additivity is only 0.17 kcal/mol. It thus appears that these all-electron calculations lend strong support to the original PPP and Hückel results. Haddon and Starnes have also considered this question of additivity and found a very similar degree of additivity when they used their STO-3G results in which all internal coordinates were assigned standard values.[17] However, when C–C bond lengths were optimized[17] the deviation from additivity in the series butadiene, hexatriene, and octatetraene increased to 2.5 kcal/mol. It is gratifying that complete geometry optimization with the 3-21G and 6-31G* bases again lowers this deviation to the acceptable value of 0.17 kcal/mol. We estimate[16] that our Hückel predictions of resonance energy per π electron (REPE) are reliable to $\pm 0.005\beta$. With $\beta = -32.74$ kcal/mol,[16] this corresponds to an error of ±0.16 kcal/mol. In going from one linear polyene to the next, two carbon atoms and two π electrons are added to the chain. Thus our 0.17 kcal deviation from additivity in the 3-21G results is equivalent to an error of $0.17/(2 \times 32.74) = 0.003\beta$ in REPE which is consistent with the estimated error in our Hückel results.

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Table III. Negative Orbital Energies of Filled Orbitals in the 3-21G Basis[a]

cyclobutadiene		benzene		butadiene		hexatriene		octatetraene		decapentaene	
$1b_{2g}$	0.29 (0.27)	$2e_{1g}$	0.34 (0.33)	$1b_g$	0.33 (0.32)	$2a_u$	0.30 (0.29)	$2b_g$	0.28	$3a_u$	0.27
$3b_{2u}$	0.44 (0.44)	$1e_{1g}$	0.34 (0.33)	$1a_u$	0.45 (0.44)	$1b_g$	0.40 (0.39)	$2a_u$	0.37	$2b_g$	0.34
$1b_{3u}$	0.48 (0.47)	$6e_{2g}$	0.49 (0.49)	$7a_g$	0.48 (0.49)	$1a_u$	0.47 (0.46)	$1b_g$	0.44	$2a_u$	0.41
$4a_g$	0.54 (0.53)	$5e_{2g}$	0.49 (0.49)	$6b_u$	0.54 (0.54)	$10a_g$	0.48 (0.49)	$13a_g$	0.48	$1b_g$	0.46
$3b_{1u}$	0.57 (0.55)	$1a_{2u}$	0.51 (0.50)	$6a_g$	0.56 (0.56)	$9b_u$	0.51 (0.51)	$1a_u$	0.48	$16a_g$	0.48
$3b_{3g}$	0.70 (0.70)	$6e_{1u}$	0.59 (0.58)	$5a_g$	0.64 (0.63)	$9a_g$	0.55 (0.54)	$12b_u$	0.50	$1a_u$	0.49
$2a_g$	0.70 (0.69)	$5e_{1u}$	0.59 (0.58)	$5b_u$	0.65 (0.64)	$8a_g$	0.57 (0.57)	$12a_g$	0.53	$15b_u$	0.49
$2b_{2u}$	0.81 (0.82)	$1b_{2u}$	0.62 (0.61)	$4b_u$	0.76 (0.75)	$8b_u$	0.61 (0.60)	$11a_g$	0.55	$15a_g$	0.51
$2b_u$	0.93 (0.91)	$2b_{1u}$	0.64 (0.64)	$4a_g$	0.82 (0.82)	$7b_u$	0.64 (0.63)	$11b_u$	0.56	$14b_u$	0.54
$2a_g$	1.16 (1.16)	$3a_{1g}$	0.72 (0.71)	$3b_u$	1.01 (1.00)	$7a_g$	0.67 (0.66)	$10b_u$	0.60	$14a_g$	0.55
$1b_{3g}$	11.19 (11.23)	$4e_{2g}$	0.83 (0.82)	$3a_g$	1.09 (1.09)	$6a_g$	0.76 (0.76)	$10a_g$	0.62	$13a_g$	0.50
$1b_{2u}$	11.19 (11.23)	$3e_{2g}$	0.83 (0.82)	$2a_g$	11.17 (11.22)	$6b_u$	0.76 (0.76)	$9a_g$	0.66	$13b_u$	0.58
$1b_{1u}$	11.19 (11.23)	$4e_{1u}$	1.02 (1.01)	$2b_u$	11.17 (11.22)	$5b_u$	0.84 (0.84)	$9b_u$	0.67	$12b_u$	0.63
$1a_g$	11.19 (11.23)	$3e_{1u}$	1.02 (1.01)	$1a_g$	11.18 (11.23)	$5a_g$	0.99 (0.99)	$8a_g$	0.75	$12a_g$	0.63
		$2a_{1g}$	1.16 (1.15)	$1b_u$	11.18 (11.23)	$4b_u$	1.06 (1.06)	$8b_u$	0.77	$11a_g$	0.66
		$1a_{1g}$	11.17 (11.23)			$4a_g$	1.11 (1.11)	$7b_u$	0.78	$11b_u$	0.68
		$2e_{1u}$	11.18 (11.23)			$3a_g$	11.17 (11.22)	$7a_g$	0.86	$10b_u$	0.75
		$1e_{1u}$	11.18 (11.23)			$3b_u$	11.17 (11.22)	$6b_u$	0.98	$10a_g$	0.76
		$2e_{2g}$	11.18 (11.23)			$2a_g$	11.18 (11.23)	$6a_g$	1.04	$9b_u$	0.77
		$1e_{2g}$	11.18 (11.23)			$2b_u$	11.18 (11.23)	$5b_u$	1.09	$9a_g$	0.80
		$1b_{1u}$	11.18 (11.23)			$1b_u$	11.18 (11.23)	$5a_g$	1.12	$8b_u$	0.86
						$1a_g$	11.18 (11.23)	$4a_g$	11.17	$8a_g$	0.98
								$4b_u$	11.17	$7b_u$	1.03
								$3a_g$	11.18	$7a_g$	1.07
								$3b_u$	11.18	$6b_u$	1.10
								$2a_g$	11.18	$6a_g$	1.12
								$2b_u$	11.18	$5a_g$	11.17
								$1a_g$	11.18	$5b_u$	11.17
								$1b_u$	11.18	$4a_g$	11.18
										$4b_u$	11.18
										$3a_g$	11.18
										$3b_u$	11.18
										$2a_g$	11.18
										$2b_u$	11.18
										$1b_u$	11.18
										$1a_g$	11.18

[a] Energies are in au; 6-31G* results are in parentheses.

Table IV. Energy Differences (au) in the Linear Polyenes (1)

n	E	ΔE	$\Delta^2 E$
0	−154.059459		
		−76.459 34	
1	−230.518 801		−0.000 26
		−76.459 60	
2	−306.978409		−0.000 06
		−76.459 67	
3	−383.438 086		

However, an error of 2.5 kcal/mol in the polyene additivity corresponds to an error of 0.038β in REPE. This is larger than the REPE of azulene (0.023β) and is half that of benzene (0.065β) which is the hydrocarbon of largest known REPE. It is worth remarking that even this unacceptable deviation would appear as less than $^1/_{100}$th the width of the line in Figure 1.

Another interesting observation can be made by plotting the 3-21G ΔE's in Table IV against those from Hückel calculations (Figure 2). A reasonably good straight line is obtained which indicates that Hückel π energies parallel the all-electron 3-21G energies amazingly well. This suggests that the contribution to the energy by the σ electrons closely parallels that of the π electrons and, we believe, gives further validity to the Hückel method.

Resonance Energies of Benzene and Cyclobutadiene

Haddon[18] has reported isodesmic[42] and homodesmotic[43,44] resonance energies of cyclobutadiene and benzene computed from

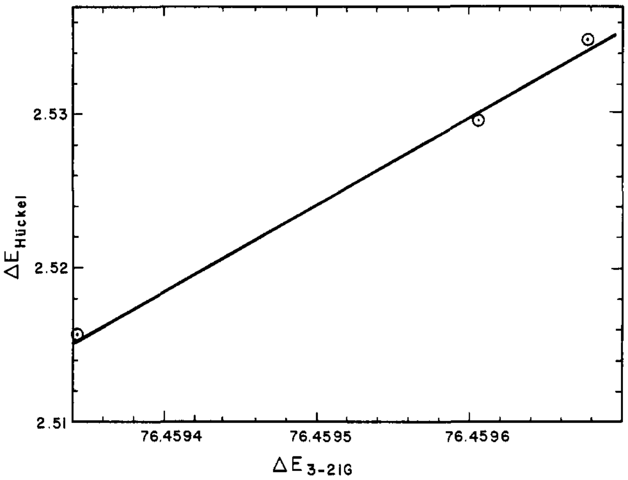

Figure 2. Energy change on going from n to $n + 1$ in the polyene series of Figure 1. Hückel energies (β) are shown vs. 3-21G results (au).

his partially optimized STO-3G wave functions. The isodesmic conjugation or resonance energy of a compound may be defined as the negative of the energy of formation of that compound from nonconjugated components in an isodesmic reaction. An isodesmic reaction has the same number of each bond type in products as in reactants. Thus eq 6 gives the isodesmic resonance energy of the [n]annulenes A_n.

$$\frac{n}{2}CH_2{=}CH_2 + \frac{n}{2}CH_3{-}CH_3 \rightarrow A_n + nCH_4 \qquad (6)$$

In this way Haddon computed 72.8 kcal/mol as the isodesmic

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(42) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

(43) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1222.

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resonance energy of benzene. Such a resonance energy corresponds at least roughly to the Hückel delocalization energy which compares the π energy of A_n to that of $n/2$ isolated double bonds. However, in addition to the π electron changes, $n/2$ sp^3–sp^3 single bonds are transformed to sp^2–sp^2 single bonds in eq 6, and these σ effects are not usually considered part of the delocalization energy.

These σ effects are taken into account by replacing the isodesmic eq 6 by a homodesmotic reaction such as eq 7, as suggested by George, Trachtman, Bock, and Brett.[43]

$$\frac{n}{2}CH_2{=}CH{-}CH{=}CH_2 \rightarrow A_n + \frac{n}{2}CH_2{=}CH_2 \qquad (7)$$

With the homodesmotic eq 7 Haddon found the resonance energy of benzene to be lowered from the isodesmic value of 72.8 to 30.3 kcal/mol. In addition to the σ effects there is a second important difference between eq 6 and 7. The sp^2–sp^2 σ bonds on both sides of eq 7 are part of conjugated systems. Hence, although they are formally written as single bonds, they have significant π character. It appears that this π contribution to formal single bonds is the crucial aspect in Dewar's[1] polyene reference structure for aromaticity. Consequently, the homodesmotic resonance energy from eq 7 is a Dewar-type resonance energy.

In studying the energy additivity of conjugated acyclic hydrocarbons and hence in the definition of the aromatic reference structure, Dewar[1] in his Pariser–Parr–Pople calculations found it necessary to distinguish only between carbon–carbon single and double bonds. On reexamining the same problem with the Hückel method, we[3] had to use five types of double and three types of single bonds depending upon the number and arrangement of the attached hydrogen atoms. George's[43] definition of a homodesmotic reaction is somewhat more restrictive than required to give a resonance energy as defined by Dewar[1] but not restrictive enough to accord with our definition.[3] For example, there are $n/2$ $CH{-}CH$ bonds on both sides of eq 7; but the n $CH_2{=}CH$ bonds on the left are replaced by $n/2$ $CH_2{=}CH_2$ and $n/2$ $CH{=}CH$ bonds on the right. One can define a still more restricted reaction type such as eq 8 in which the bond types, as we have defined

$$\frac{n}{2}CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2 \rightarrow A_n + \frac{n}{2}CH_2{=}CH{-}CH{=}CH_2 \qquad (8)$$

them,[3] are conserved. In eq 8 there are n $CH_2{=}CH$, n $CH{-}CH$, and $n/2$ $CH{=}CH$ bonds in both reactants and products. These reactions might be called (with apologies to George and coworkers) "hyperhomodesmotic". It can be shown easily that for hydrocarbon reactions "hyperhomodesmotic" is a subclass of "homodesmotic" which is a subclass of "isodesmic". Using eq 7 our 3-21G results in Table I give a homodesmotic resonance energy for benzene of 27.6 kcal/mol (6-31G*: 24.7 kcal/mol) in good agreement with Haddon's result, and eq 8 gives a 3-21G hyperhomodesmotic resonance energy of 26.0 kcal/mol (6-31G*: 23.4 kcal/mol) which is not significantly different.

Although the homodesmotic (corresponding to Dewar's two bond types) and hyperhomodesmotic (corresponding to our eight bond types) resonance energies are nearly equal in this example of benzene, this is not true in general. Consequently all resonance energies discussed below will be of the hyperhomodesmotic type. A confusing point of nomenclature is that we have in the past described (and wish to continue to describe) both the homodesmotic and hyperhomodesmotic resonance energies as "Dewar-type" resonance energies in spite of the fact that Dewar himself used only two bond energies (homodesmotic). The point is that both include π contributions to the single bonds in the reference structure, and this we think is the key to the success of the polyene reference. The important contrast is then between Dewar-type resonance energies (homodesmotic or hyperhomodesmotic) using a polyene reference and standard delocalization energies using an isolated $C{=}C$ reference (isodesmic). Further, rather than use the energy of specific $CH{=}CH$ and $CH{-}CH$ bonds as in eq 8, we shall use an "average" value obtained for the polyene reference from the series **1** and presented in Table I and Figure 1 to obtain annulene resonance energies by eq 9.

$$RE(A_n) = E(A_n) - n(E_{CH=CH} + E_{CH-CH}) \qquad (9)$$

Table V. Ab Initio Resonance Energies (kcal/mol) of Cyclobutadiene and Benzene

	3-21G	6-31G*
benzene		
total resonance energy	25.6	23.4
H···H correction	+0.054	+0.024
ring strain correction	0	0
π resonance energy	25.7	23.4
cyclobutadiene		
total resonance energy	−92.6	−85.4
H···H correction	−1.3	−1.3
ring strain correction	+32.0	+32.0
π resonance energy	−61.9	−54.7

First it is necessary to consider features of this polyene reference that were neglected in the earlier Hückel treatment.[3] As n is increased by one in the polyene series **1**, a $-(CH)_2-$ unit with trans hydrogen atoms is added to the chain. In the annulene series the analogous building block contains cis hydrogens. This difference produces no effect in either the Hückel or PPP treatments, but it does in the ab initio results. Similarly, the Hückel and PPP calculations ignore ring strain which is automatically included in ab initio wave functions. Two approaches might be taken in defining ab initio Dewar-type resonance energies. Resonance energies might be defined as the difference between the energy of the molecule in question and the energy of the polyene reference with no allowance for differences in nonbonded interactions or ring strain. This "total resonance energy" would be formally analogous to what was obtained in the successful Hückel method, and could be rigorously computed. The difficulty is that such resonance energies would include contributions from σ-electron effects and there is some feeling that resonance energy should be a phenomenon involving only the π electrons. The σ contributions might be estimated with empirical potential functions, but there is considerable uncertainty in what are the best potential functions. Hence "π resonance energies" computed in this way would be somewhat arbitrary. Further, if ring strain and H···H nonbonded interactions are to be considered, should not nonbonded interactions between all other atom pairs, σ bond compression energy, and perhaps other vaguely defined energy effects also be taken into account? These questions cannot yet be answered in an a priori way since it is not yet understood even why, in the Hückel method, the Dewar-type resonance energies (using a polyene reference) give better predictions of aromaticity than do the older delocalization energies (using an ethylene reference). Accordingly, we shall compute both total resonance energies and π resonance energies for benzene and cyclobutadiene as a first step in determining which is more useful.

A least-squares fit of the straight line in Figure 1 gives as the slope −76.459 549 au. This is the energy of the $-(CH)_2-$ reference unit. Hence the total reference energy of benzene is simply 3 × −76.459 549 au = −229.378 647 au. The resonance energy of benzene is therefore +229.419 451 au − 229.378 647 au = +0.040 804 au or 26 kcal/mol in the 3-21G basis. Similarly, using the difference in the 6-31G* energies of 1,3-butadiene and 1,3,5-hexatriene and the 6-31G* energy of benzene gives 23 kcal/mol for the 6-31G* total resonance energy of benzene.

In both the 3-21G and 6-31G* calculations neighboring hydrogens are slightly closer in benzene than in the reference structure. This will decrease the total resonance energy slightly in comparison with the π resonance energy. We have used the Hill potential,[46] as recommended by Allinger, Miller, Van-Catledge and Hirsch[47] for the interaction of two nonbonded hydrogen

$$E(H\cdots H) = [-0.225(2.9/R)^6 + 0.828 \times 10^5 \exp(-R/0.21344)] \text{ kcal/mol} \qquad (10)$$

atoms separated by a distance of R. As shown in Table V, these interactions make only a negligible contribution to the resonance energy of benzene. Equation 10 is only one of several potentials suggested in the literature, but it is one of the "hardest" (see Figure 2 of ref 48). Most others would give an even smaller estimate of the effect of H···H interaction. The six-membered ring was assumed to be strain free. No other effects were considered, so that the total and π resonance energies are nearly identical. This ab initio value of the Dewar resonance energy is roughly double the 13 kcal/mol Hückel estimate of the same quantity.[16] It is in fairly good agreement with Dewar's own Pariser–Parr–Pople value of 20 kcal/mol.[1] Correlation effects have not been included in these calculations; they might be expected nearly to cancel between a molecule and its reference.

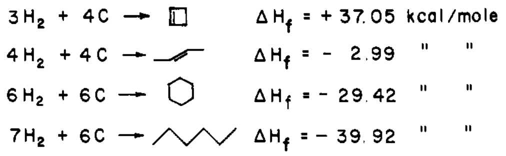
A similar treatment for cyclobutadiene gives the total resonance energies in eq 11 (3-21G) and eq 12 (6-31G*). Both basis sets

$$\text{RE} = -152.7715 \text{ au} - 2(-76.459549 \text{ au}) = -0.147584 \text{ au} = -92.6 \text{ kcal/mol} \quad (11)$$

$$\text{RE} = -153.641117 \text{ au} - 2(-76.888620 \text{ au}) = -0.136123 \text{ au} = -85.4 \text{ kcal/mol} \quad (12)$$

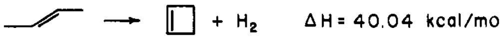
indicate a large cyclic destabilization, that is, a high degree of antiaromaticity, in cyclobutadiene; and the 3-21G result is in exact agreement with Haddon's[18] homodesmotic resonance energy. Neighboring hydrogen atoms in cyclobutadiene are more distant than those in benzene and, by eq 10, lie in the van der Waals' attraction region. Consequently, the effect is in the opposite direction from that in benzene. As seen in Table V, the H···H energy is larger in cyclobutadiene than in benzene, but it is still only a small part of the total resonance energy.

Ring strain energy in cyclobutadiene is certainly significant, and some estimate of its magnitude needs to be made. Consider the following heats of formation[49] (eq 13–16):



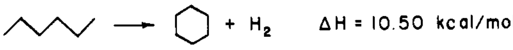
(13)
(14)
(15)
(16)

Subtraction of eq 14 from eq 13 gives



(17)

and eq 15 minus eq 16 gives



(18)

Hence if one considers cyclohexane to be strain free, the strain energy of cyclobutene is 40.04 − 10.50 = 29.54 kcal/mol which compares favorably with that obtained by Wiberg (28.4 kcal/mol).[50] A similar treatment of cyclobutane yields 26.64 kcal/mol as its strain energy. Note that the introduction of a double bond into the ring of cyclobutane causes only a slight increase in the strain energy. One therefore might argue that the introduction of a second double bond, as in cyclobutadiene, will cause a similar small increase in strain. This gives an estimated strain energy for cyclobutadiene of 32 kcal/mol, which compares favorably with the estimate of the four-membered ring strain energy in biphenylene (27.5 kcal/mol) made by Dewar[51] and de Llano.[52]

Correcting the total resonance energy for ring strain and H···H interactions in Table V gives the π resonance energy of cyclobutadiene to be −62 kcal/mol in the 3-21G basis and −55 kcal/mol in the 6-31G* basis.

It has been shown above that the Hückel π energies of the linear acyclic polyenes parallel the ab initio total energies remarkably well. Is there a similar parallel in π resonance energies of the two methods? The ratio of ab initio π resonance energies of cyclobutadiene to benzene is −2.3. In the Hückel method this ratio is −1.07/0.39 or −2.74. This agreement is not nearly as good as that found for the energies of the linear polyenes. However, it can be argued that the antiaromaticity of cyclobutadiene is overestimated by the Hückel method since it is assumed in that method that cyclobutadiene has equal bond lengths whereas the optimized ab initio geometries show a strong distortion away from the square to lower the cyclic destabilization. It is also true that these ratios are closer to each other than to the ratio of ab initio total resonance energies (−3.6).

In summary, it has been shown that the additivity of linear polyene energies, first shown by Dewar in the PPP method and later by us for the Hückel method, also holds in reasonably good all-electron calculations. An outcome of this is that it has been possible to obtain ab initio resonance energies of benzene and cyclobutadiene based on a Dewar reference structure.

Registry No. Butadiene, 106-99-0; hexatriene, 2235-12-3; octatetraene, 1482-91-3; decapentaene, 2423-91-8; cyclobutadiene, 1120-53-2; benzene, 71-43-2.

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