Do the C—H Bonds Contribute to the Stabilization Energy of Benzene?*

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The stabilization energy of benzene (*SE*) is proposed to be
calculated from the increments of heats of formation in the homo-
logous series of conjugated polyenes. In this way 19.7 and 23.0
kcal/mol* are derived for SE, when benzene is compared to *trans*
and *cis* type polyenes, respectively. A comparison of the estimated
C—C bond energy of benzene to that of olefins leads to the conclus-
ion that C—C bonds are responsible for only about 2/3 of *SE*. It is
suggested that the rest of SE is connected with the difference in
strength of the aromatic and olefinic C—H bonds.

The stabilization energy of benzene (*SE*) has long been defined as the dif-
ference between the heat of formation (ΔH_f) of benzene and that of a hypo-
thetic reference compound: 1,3,5-cyclohexatriene. Since this compound does
not exist, its ΔH_f, of course, can not be determined experimentally. The
reference ΔH_f has usually been calculated from empirically or theoretically
derived bond energies. In this way, for example, Klages[1] and Dewar[2] suggested
35.9 and 20 kcal/mol for the *SE*, respectively.

In order to avoid uncertainties due to the non-existence of the reference
compound, the authors of the present paper suggest that the definition and
calculation of *SE* be based on experimentally determined ΔH_f-s of conjugated
polyenes. ΔH_f increments can be derived from the ΔH_f-s of neighbouring
members of the homologous series of linear open chain conjugated polyenes.
A ΔH_f increment may be considered as a contribution of two =CH— groups
to ΔH_f-s. Since benzene consists of six =CH— groups, a threefold value of the
ΔH_f increment can well be accepted as a reference ΔH_f for the calculation
of *SE*.

At present, gas phase ΔH_f-s are only available for the first three members
of the homologous series: ΔH_f-s of ethylene[3], 1,3-butadiene[3], trans- and cis-
-1,3,5-hexatriene[4] are 12.5, 26.33, 39.5 and 40.6 kcal/mol, respectively. The
increments derived from these data — marked as $\Delta H_f (=CH—)_2$ — are shown
in Table I. Increment No. 1 is calculated by subtracting the ΔH_f of ethylene

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* Presented in part at the International IUPAC Symposium on Aromaticity,
held in Dubrovnik, Croatia, Yugoslavia, September 3—5, 1979.

* In our calculations 1 kcal/mol = 4.184 kJ/mol.

TABLE I

Calculated ΔH_f Increments and Stabilization Energies

Incr. No.	Chain type	$\Delta H_f/=CH—/_2$ kcal/mol	$\Delta H_f/=CH—/_6$ kcal/mol	SE kcal/mol
1.		13.83	41.49	21.67
2.	trans	13.17	39.51	19.69
2.	cis	14.27	42.81	22.99

from that of butadiene. Increment No. 2 comes from ΔH_f-s of butadiene and hexatriene. This result, however, is dependent on the trans or cis structure of hexatriene. The increment belonging to the trans structure is somewhat lower, while the one characterizing the cis chain is somewhat higher than increment No. 1. Perhaps it is worthwhile to note that the mean value of the two No. 2 increments (13.72 kcal/mol) is almost equal to increment No. 1.

The stabilization energy of benzene was calculated by subtracting ΔH_f of benzene (19.82 kcal/mol)[3] from the threefold values of ΔH_f increments $/\Delta H_f (=CH—)_6/$. Results are also shown in Table I. As it is seen, the stabilization energy, when benzene is compared to a trans type polyene, is 19.7 kcal/mol. If, however, the comparison is made between benzene and a polyene with cis structure, the SE is higher: 23.0 kcal/mol. Either of these two values of SE can be used to characterize the extra stabilization of benzene over polyenes if the structure of the polyene (cis or trans) is indicated. It is unlikely that the availability of ΔH_f-s of higher members of the homologous series in the future would substantially modify these figures.

Generally, the C—C bonds are considered to be the source of SE. Therefore it seemed interesting to make an estimation of the difference between the C—C bond energy of benzene and that of polyenes /calculating with 3 double and 3 single bonds/, and to compare the result with the previously calculated SE. To carry out this estimation, an empirical formula has been set up for calculating the C—C bond energy from experimentally determined bond distances:

$$E_{CC} = 431.9 — 224.3 \ R_{CC}$$

where E_{CC} and R_{CC} are the bond energy (in kcal/mol) and bond distance (in Ångströms), respectively. The constants were calculated from the experimental bond distances and heats of atomization of diamond and graphite*. The equation is supposed to be valid as far as the C—C bonds of alkanes, alkenes and the aromatic hydrocarbons are concerned and there is no angle distortion.

As an example, C—C bond energies of some simple hydrocarbon molecules were calculated and are shown in Table II. All these molecules have only one kind of C—H bond. These C—H bond energies were calculated by subtracting the sum of C—C bond energies (if any) from the heat of atomization (A) and

* The heat of atomization of graphite was decreased by 1.6 kcal/mol to make an allowance for the estimated value of binding energy between the layers.

TABLE II

Calculated C—C and C—H Bond Energies

	R_{CC} exper.[5]	E_{CC} calc.	A^* exper.	E_{CH} calc.	$\nu/CH/^{is}$ exper.[6]
	Å	kcal/mol	kcal/mol	kcal/mol	
methane	—	—	397.6	99.4	2992
ethane	1.533	88.0	675.4	97.9	2950
ethylene	1.337	132.0	538.5	101.6	3055
benzene	1.399	118.1	1320.5	102.0	3065

* The heats of atomization were calculated using experimental heats of formation[3].

by dividing the result with the number of C—H bonds. In the last column of Table II the experimental — so called »isolated« — IR stretching frequencies are indicated. It can be easily shown that there is a very good linear relationship between the calculated E_{CH}-s and the observed $\nu(CH)^{is}$-s. This may be considered as an indirect support for the validity of the empirical equation introduced above.

The C—C bond distances of a reference conjugated polyene were estimated from the experimental C—C bond lengths of ethylene and 1,3-butadiene[5] — regarded as quite accurately determined. The single bond distance of butadiene (1.465 Å) was directly adopted for the polyene. The double bond distance was estimated by taking into account that the double bond lengthening when going from ethylene (1.337 Å) to butadiene (1.345 Å) is 0.008 Å. Twice this value is expected when going from ethylene to an internal double bond of a polyene since in this structure two H atoms of ethylene (instead of one) are replaced by sp^2 carbons. Thus, 1.353 Å was adopted for the length of the reference double bond, which is in good agreement with the 1.351 Å calculated by Dewar for this type of bond[2].

The bond energies of the C—C bonds of the reference polyene as well as those of benzene were calculated by using the empirical formula, and the results are shown in Table III. It can be seen that the sum of the calculated C—C bond energies of the reference polyene is smaller than that

TABLE III

C—C Bond Energy of Benzene and the Reference Polyene

	Type of bonds	R_{CC} Å	E_{CC} kcal/mol	No. of bonds	ΣE_{CC} kcal/mol
polyene	C=C	1.353	128.4	3	695.1
	C—C	1.465	103.3	3	
benzene	C⋯C	1.399	118.1	6	708.4

of benzene, as expected. Their difference, however, is only 13.3 kcal/mol. This is considerably lower than the proposed experimental stabilization energies indicated in Table I. It should be noted on the other hand that the above figure is strongly supported by earlier calculations of Schaad and Hess[7]. Exactly the same value (0.577 eV equivalent to 13.3 kcal/mol) has been proposed for the total resonance energy of benzene. Taking all these into account it can be concluded that the changes in the C—C bond distances are only in part responsible for the enhanced stability of benzene. Roughly, only 2/3 of *SE* arises from the overall strengthening of the C—C bonds and this implies that the rest must be somehow connected with the C—H bonds. In other words, the C—H bonds of benzene are probably stronger than those belonging to a =CH— group of a conjugated polyene, and so, the strengthening of the 6 C—H bonds is the source of about 1/3 of *SE*.

Unfortunately, at present, there is no direct experimental evidence to prove this conclusion (although it should be noted that, as far as the authors are aware, there is no experimental support for the equivalency of the C—H bonds, either). The individual (»isolated«) stretching frequencies of polyenes have not yet been determined. It is worthwhile, however, to consider the known »isolated« stretching frequencies of propene indicated in Figure 1. Taking into consideration the relationship between E_{CH} and ν (CH)^{is} (Table II), Figure 1 clearly demonstrates that the C—H bond in the =CH— group of propene is considerably weaker than those belonging to the terminal
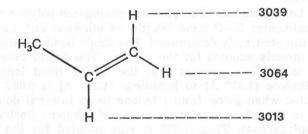

Figure 1. IR stretching frequencies (cm⁻¹) of the olefinic C—H bonds in propene[6].

=CH₂ group of the same molecule. The estimated* difference is 1.3—1.4 kcal/mol/bond. If this tendency holds for conjugated polyenes, too, it supports the above conclusion that the strengthening of the C—H bonds do contribute to the stabilization energy of benzene.

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* The calculation is based on the mean value (3052 cm⁻¹) of the two terminal C—H stretching frequencies. It may be worthwhile to note that this value is very close to the stretching frequency of ethylene.

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SAŽETAK

Da li C—H veze doprinose energiji stabilizacije benzena?

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Predloženo je da se energija stabilizacije benzena (*SE*) računa iz doprinosa toplina stvaranja homolognog niza konjugiranih poliena. Na taj su način, usporedbom benzena sa polienima trans i cis tipa dobivene za *SE* vrijednosti od 19.7 i 23.0 kcal/mol, respektivno. Usporedba procijenjenih energija C—C veze u benzenu i olefinima vodi do zaključka da su C—C veze odgovorne tek za oko 2/3 *SE*. Sugerira se da bi ostatak od *SE* bio povezan sa razlikom u jakosti aromatskih i olefinskih C—H veza.

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