ANALYSIS OF THE ELECTRON DENSITY AND POTENTIAL OF SOLID BENZENE

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ABSTRACT.—The electron density distribution of the benzene molecule is analyzed in terms of the selected electron shell (SES) method. With this method the electron density is split into two terms corresponding to the inner and outer electrons, respectively. The validity of subtracting a Gaussian distribution for the inner electrons is checked against the equivalence of subtracting the ls^2 contribution. The potential function for the benzene crystal is calculated from experimental x-ray diffraction data. A low potential barrier is observed between the atoms in the benzene ring indicating the presence of delocalized electrons. Also the high potential barrier between molecules is in accordance with the idea that molecules are closed electron systems.

Benzene occupies a central position in organic chemistry and in molecular theory. The basic electronic structure of the molecule is well understood in terms of the molecular orbital theory, which in essence, considers the bonding electrons to be distributed into the α, or localized, and α, or delocalized, types. The molecule of benzene consists accordingly of a framework built up by the trigonal hybrid sp^2 orbitals of the separated atoms overlapping with themselves or with the ls orbitals of hydrogen. The linear combination of the p_z atomic orbitals of the carbon atoms build up the α molecular orbitals. The electron density of benzene has been worked out theoretically by March (1952) by applying the Thomas-Fermi and the molecular-orbital method, but there is no other analysis of the experimentally observed electron density except the work done by Cox et al. (1958). One of the problems in the study of the electron density via x-ray diffraction methods is that it is difficult to get rid of the series termination effect. Another problem is that the most important contribution to the total electron density derives from the electrons near the nucleus of the atom, forbiding any detailed analysis of the experimental maps.

In a series of papers, the authors have shown (Amoros and Canut-Amoros, 1968, 1969, 1970) that it is possible to separate the contribution of the inner and outer electrons to the atomic scattering factor. As a consequence, the analysis of the density distribution from an experimental point of view can be done. The method, that has been called the selected electron shell (SES) method, is based on the possibility of an analytical representation of the atomic scattering factor as a Gaussian polynomial of positive terms, each one corresponding to what we call an electron shell. The method proved to be powerful in the sharpening of the Patterson of a molecular crystal, and it was tested successfully in the analysis of the electron distribution of the outer electrons in hexamine. It seemed, therefore, appropriate to extend the SES analysis to the molecule of solid benzene.

CRYSTAL STRUCTURE OF SOLID BENZENE

Benzene has a fairly simple orthorhombic crystal structure, for which good x-ray diffraction data have been provided by Cox, Cruickshank and Smith (1958) from experiments at $-3°C$. Solid benzene belongs to the space group Pbca of unit cell dimensions a = 7.46, b = 9.66, c = 7.03 Å. It contains four molecules located on the centers of symmetry at 000, 0,1/2,1/2;1/2,0,

1/2, and 1/2,1/2,0, as first given by Cox (1932). The refinement of the structure by the forementioned authors gave well resolved atomic positions for the three independent carbon atoms. The positions of the hydrogen atoms were assumed to be at a radial distance of 1.084 Å from the carbon atom to which the hydrogen is associated. The atomic coordinates of the hydrogen atoms were calculated in this way by Harada and Shimanouchi (1966).

An overall reliability factor of 10.5% was obtained by Cox and collaborators after five differential cycles of refinement, introducing anisotropic temperature factors. Those temperature factors were further utilized by the same authors to determine the translational and librational components of the amplitudes of vibration of the rigid benzene molecule. The possibility of this analysis showed us that the observed amplitudes and the whole crystal structure were reliable, and that the SES method could be applied to this crystal. In our study we shall assume that the atomic coordinates as determined by Cox, Cruickshank and Smith are correct.

Application of the SES Method

In our previous work on hexamine (Amoros and Canut-Amoros, 1969) it was shown that the innermost electrons of carbon could be approximated by a Gaussian function whose G_s was taken as 2, the number of electrons in the inner shell. Also it was shown that the parameter g's, which contains both the form and temperature factors of the Gaussian function, can be refined by using the structure factors that correspond to reflections with $|r^*| > .9$ Å^{-1}. The SES method utilizes a difference Fourier summation of the type

$$\rho_{outer}(r) = \frac{1}{v} \sum_h (F_{obs} - (F_{inner}) \exp(2\mu i\, r.r_h^*) \quad (|r_h^*| \leq R_L^* \lim) \qquad (1)$$

where v is the unit cell volume, F_{obs} are the observed structure amplitudes, and F_{inner} are the calculated structure amplitudes for the inner electrons alone. Eq. (1) can be calculated by evaluating the contribution of the inner electrons once the parameter g'inner has been determined for each independent carbon atom. In the case of benzene 110 observations were used in the region of the reciprocal space beyond $|r^*| = .9$ A°$^{-1}$. In the refinement of ginner the accepted atomic coordinates were used. The contribution of the hydrogen atoms in this region of reciprocal space is negligible and it was disregarded. Equation (1) is then calculated using all terms within a region of the reciprocal space limited by a sphere of radius $|r^*| = 1.$A°$^{-1}$, the limit of influence of the outer electrons of carbon. Series (1) contains therefore the contribution of the outer electrons of carbon and the hydrogen atoms and is free of series termination effect.

Once the Gaussian functions that describe the electron density of the inner electrons are known, the electron density distribution of the inner electrons in the benzene molecule can be calculated either by convolution or by a Fourier summation of the normal type whose coefficients are the calculated ones. Due to the high temperature factor of the carbon atoms in benzene, the Fourier series method is applicable. The series is practically convergent, and no important series termination effect is observed as

discussed later on. Finally, the density map of the outer electrons of the carbon atoms alone can be calculated by subtracting from Eq. (1) the contribution of the hydrogen atoms.

At this stage one may question the legitimacy of subtracting a Gaussian function as the corresponding function of the electron distribution of the innermost electrons in carbon. In benzene we have the carbon 1s, 2s, and 2p, and the hydrogen 1s functions. The approximation used by the SES method must be equivalent to subtract the 1s state of carbon. In order to be sure that this is the case, the contribution of the 1s function was subtracted using the values of the shell scattering of 1s 1/2 given by Cromer and Waber (1964) taking into account that two electrons belong to this state. The procedure followed in this new calculation was similar to the previous one. First the anisotropic temperature factors for the 1s shell were deter-

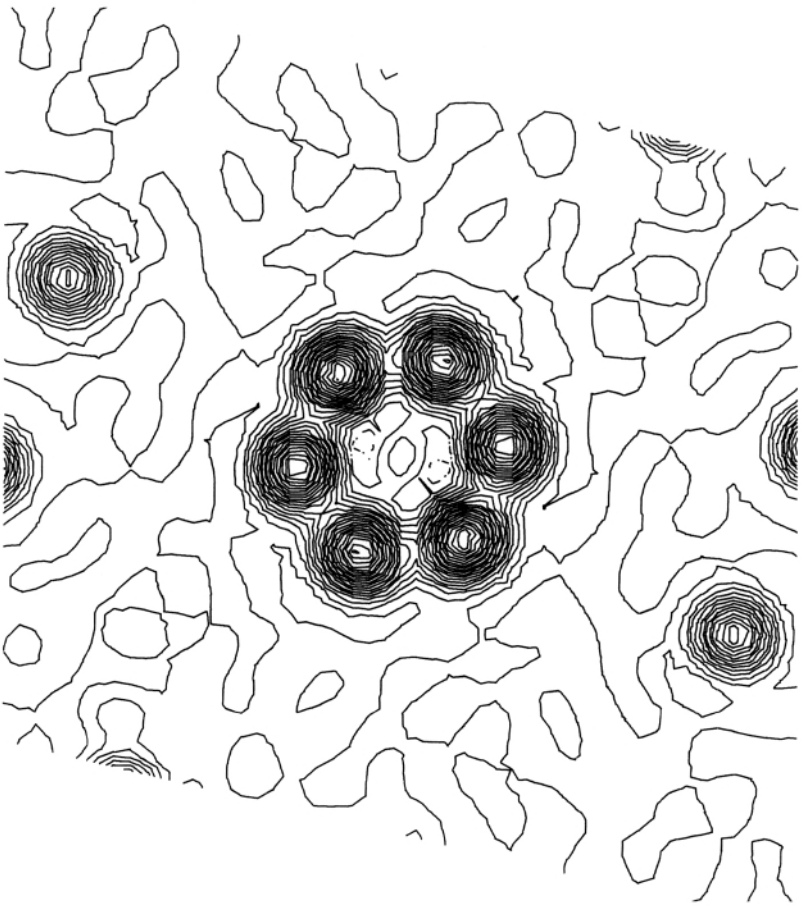

FIGURE 1a. Electron density distribution of benzene. Section through the molecular plane. Contour lines at increments of 0.2 e A^{-3}. Linear scale 1 cm = 1A. Carbon inner electrons only. The first contour line 0.0 e A^{-3} is not significative.

mined using the observed values for $|r^*| > .9$ A°$^{-1}$. Then a difference Fourier series of the type of Eq. (1) was performed in which the F_{inner} were computed in terms of the 1s electrons alone.

Analysis of the Results

The most interesting maps are those corresponding to the section through the molecular plane. According to our theory, the electron density can be split into two terms: the inner and outer electron density. Figure 1 gives the SES maps.

The first map (Fig. 1a) corresponds to the inner electrons. The zero line is very well defined, and no values higher than than 0.1 e. A°$^{-3}$ are observed in the map outside the molecule. The fluctuation

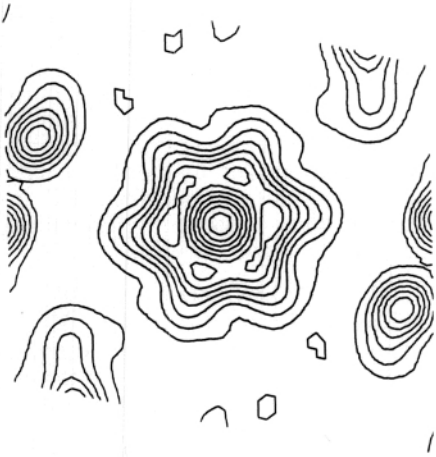

FIGURE 1b. Benzene outer electrons (a Gaussian core for carbon atoms has been subtracted). First contour line 0.2 e A-^{3}.

of the background is so small that the map is practically free of series termination effect. The electron density shows maxima of about 3.65 e. A°$^{-3}$ centered at the sites of the six carbon atoms of the molecule. Thermal motion causes an overlap of the electron density at mid-point between two adjacent carbon atoms, and due to this a reading of 0.9 e. A°$^{-3}$ is observed at that mid-point.

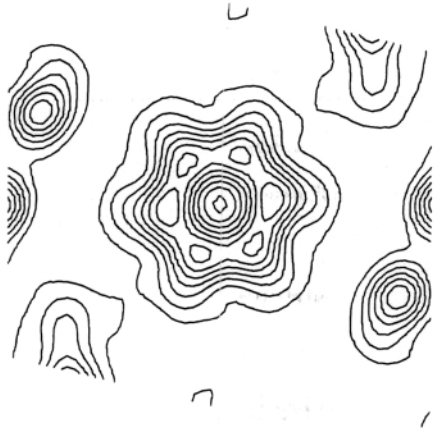

FIGURE 1c. Benzene outer electrons (1s isotropic state for carbon atoms has been subtracted). First contour line 0.2 e A-^{3}.

The outer electrons density maps are particularly interesting. Two kinds of maps have been computed. One map was calculated subtracting only the inner electrons as given by the Gaussian approximation (Fig. 1b). The map contains then the electron distribution of the outer electrons of carbon and the hydrogen electron. The map clearly shows the distortion of the basic hexagon of carbons produced by the presence of hydrogens. It is interesting to note that the outer electrons of carbon behave like a doughnut of almost constant density of about 1.4 e. A°$^{-3}$ showing very small maxima of 1.5 e. A°$^{-3}$. In order to check the validity of the Gaussian approximation for the inner electrons, a similar map was computed by subtracting the contribution of the 1s orbital. The resulting map (Fig. 1c) is identical to the previous one (Fig. 1b), the only difference being that the small maxima of 1.5 e. A^{-3} at the atomic positions are more de-

fined. The size of the van der Waals envelope and distribution of contour lines is identical in both cases, as well as the count of 0.2 e. A^{-3} at the center of the benzene ring. From this follows that the Gaussian approximation for the inner electrons is a realistic one. The maps are very similar to the ones calculated by March (1952), corresponding to the molecular orbital electron-density contours in a plane parallel to the plane of the ring at a height of 0.35 Å above the plane of the ring, which could be expected from the averaging effect of thermal vibration in the real molecule.

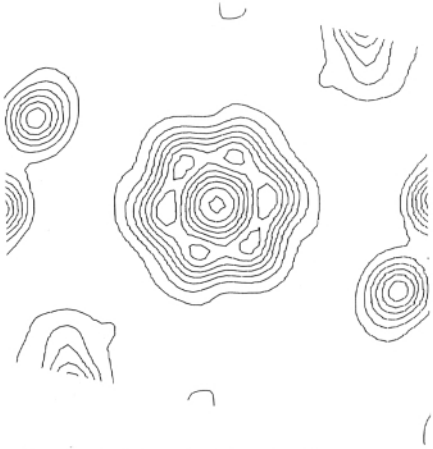

FIGURE 1d. Carbon outer electrons only. First contour line 0.2 e A^{-3}.

The last map corresponds to the outer electrons of the carbon atoms alone (Fig. 1d). In the calculations the contribution of the inner electrons of the carbon and the hydrogen atoms have been subtracted. The consequences of existing delocalized electrons is the existence of a region of almost constant electron density. In fact, the map shows very clearly that this is the case in benzene. It is important to note that the subtraction of the hydrogen atoms did not alter the electron density in the benzene ring nor the inner part, and only the humps due to the hydrogen atoms have disappeared.

Better information can be obtained by observing the graph of Fig. 2. In the graph the electron density in the plane of the molecule has been plotted along a radial line uniting two opposite carbon atoms of the ring. The electron density curves of the inner, outer and hydrogen electrons are clearly visible. Also, the positions of the C and H as deduced from x-rays by Cox, Cruikshank and Smith (1958) and neutron diffraction experiments by Bacon, Curry and Wilson (1964) are included. Thermal motion forces the observed peak positions of the carbon atoms as determined from x-ray experiments to move toward the center of the benzene ring. It is rewarding to note that the zero electrons contour line in our maps coincide with the effective size of the van der Waals envelope for carbon atoms or for hydrogen + carbon atoms determined from the intermolecular potential (Newman, private communication).

THE POTENTIAL FUNCTION

The study of the nature of the chemical bond can also be conveniently done by analyzing the potential distribution in the unit cell. It was shown by Ewald (1938) and Laue (1940) that the electrostatic potential can be calculated from the Fourier series

$$(r) = \frac{e}{\eta v} \sum_h \frac{F_h}{r^{*2}_h} \exp\left(2\eta i\, r.r^*_h\right) \quad (2)$$

where e is the electron charge. This series has the advantage that converges very rapidly, especially in molecular compounds where the temperature factor is normally high. Further advantage of Eq. (2) is that it can be calculated directly from

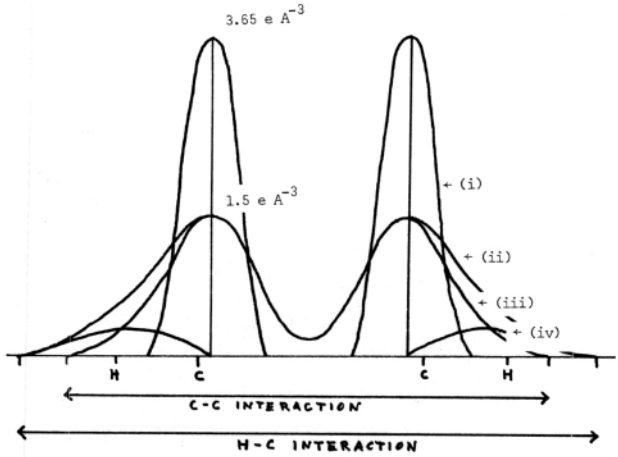

FIGURE 2. Electron density along two diametrally opposite carbon atoms. Linear dimension 1 cm = 1A.

(i) Inner electrons of carbon atoms only.
(ii) Outer electrons with hydrogen atoms.
(iii) Outer electrons without hydrogen atoms.
(iv) Electron density of hydrogen atoms.

experimental data. Series (2) has been used for the analysis of the potential in semiconductors (see, for instance, papers published in Sirota (1968). However, no calculations have been done for molecular crystals, although this kind of function has great interest because it gives the experimental form of the van der Waals envelope of a molecule and enables the determination of the potential barrier between molecules. With this in mind, the observed potential function for benzene was computed.

The most significant map is the section through the molecular plane, which is given in Fig. 3. The atomic positions are determined by well defined potential wells separated by low potential barriers. The barrier has a potential of 1.6 eV. The low value of the potential barrier is in agreement with the view of existence of delocalized electrons in the benzene ring. The center of the molecule shows a barrier of 4.8 eV. with respect the atomic well, which indicates the possibility of some electron density in the center of the molecule. This is in agreement with the SES map of the outer electrons that shows an electron density of 0.2 e. A^{-3} at that point.

One of the most interesting features of the map is the clear limitation of the benzene molecule, that is bound by a high potential barrier. The lowest value of this barrier corresponds to about 14 eV with respect to the atomic positions. This value corresponds to the line along the nearest intermolecular distance in the plane of the section. This indicates that strong repulsion between the electron clouds of neighboring molecules exist and that the molecule must be considered as a closed system of electrons in agreement with current ideas of molecular crystals.

The value of the potential and potential barriers obtained from Eq. (2) depends upon the temperature factor. Therefore, the actual values given here must be taken as

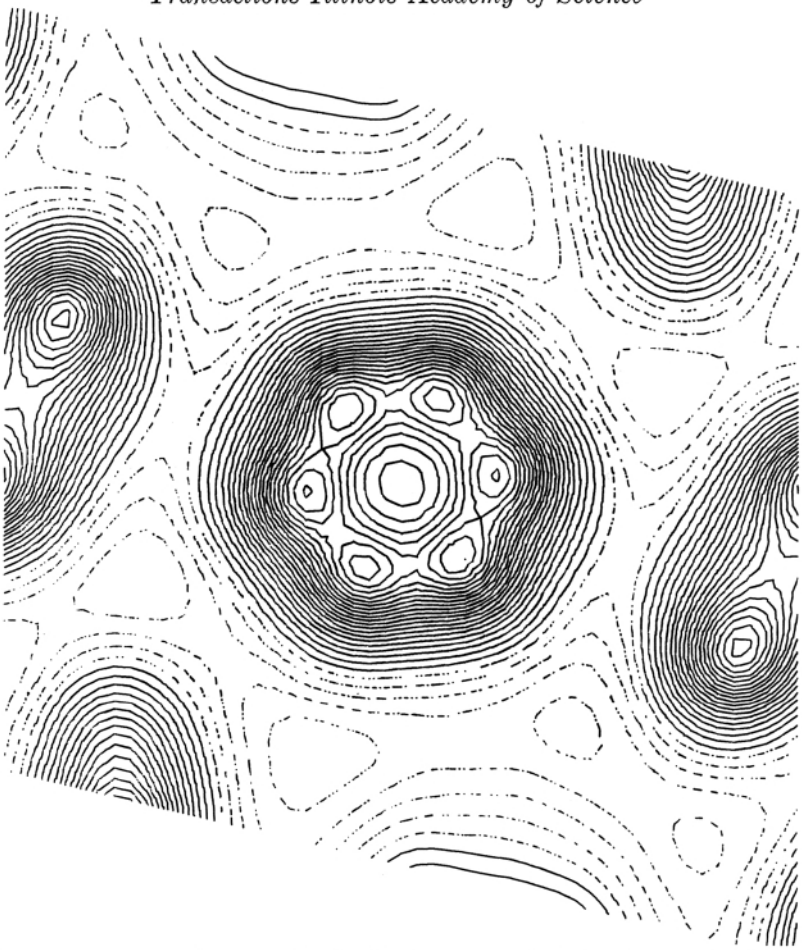

FIGURE 3. Electronic potential distribution through the benzene molecular plane. The first continuous line corresponds to O e V. Contours at increments of 0.3 e V.

having qualitative rather than quantitative significance. However, a significative picture of the existence of low and high potential barriers can be obtained from electron-potential maps.

The study of intermolecular potential barriers is of great interest for a better understanding of the chemistry of molecular solids. Further work on this sense is therefore necessary.

COMPUTATIONAL WORK

The computational work was made in an IBM 7044 and the plots in the digital incremental CalComp 565 plotter with off-line magnetic tape unit 470.

The least squares refinements and structure factor calculations were done with the ORFLS program of Busing, Martin and Levy (1962). The Fourier series were computed with the FORTRAN program of Zalkin (1962). Details of the actual computations involved in the SES method have been given by Canut-Amoros, Casper, Walters and Amoros (1970) and the computing

programs described in the Computing Report of Canut-Amoros et al. (1968).

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