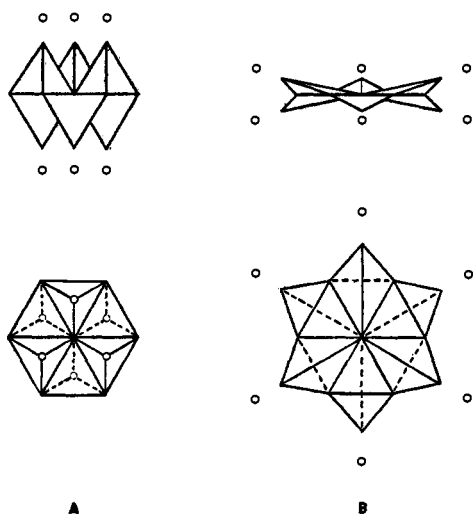


THE OSCILLATING, PUCKERED, CENTROID MODEL FOR THE BENZENE RING

Sir:

Some time ago<sup>1</sup> the writer showed that many of the peculiarities of benzene and its derivatives could be accounted for by assuming a structure for the ring like that postulated by Körner<sup>2</sup> (Fig. 1, A) except for distorted (B) rather than regular tetrahedra. (The tetrahedra represent assumed preferred orientations of valence electrons or orbits.)<sup>3</sup>

The chief argument against this structure was lack of evidence for isomers which would be expected of disubstituted benzene derivatives. It has since been shown<sup>4</sup> that predictions on the basis of that theory that so-called 1,8-disubstitution products of naphthalene would be found to be



1,5-, and *vice versa*, are incorrect. Moreover, x-ray studies of graphite<sup>5</sup> and of  $C(CH_3)_6$ <sup>6</sup> have indicated that in these substances the centers of the carbon atoms, of a single layer or molecule, lie in or nearly in one plane.

This evidence is satisfied if one assumes that the "tetrahedra" are sufficiently distorted, placing 1,8-substituents in naphthalene closer together than 1,5-substituents, and that there is frequent or constant oscillation between such a puckered form and its mirror image, preventing

the isolation of isomers and giving a time-average distribution of x-ray scattering power ("electron density") like that deduced from the observations.

Consideration of such forces as the repulsion between atomic kernels would lead one to expect a tendency toward a puckered rather than a plane ring. With only slight puckering the same factors which are responsible for molecular rotation in the solid state<sup>7</sup> might be expected to

<sup>1</sup> Huggins, *THIS JOURNAL*, **44**, 1607 (1922).

<sup>2</sup> Körner, *Gazz. chim. ital.*, **4**, 444 (1874).

<sup>3</sup> Cf. Bartlett, *Phys. Rev.*, **36**, 1096 (1930), and papers by Bartlett and by Slater at the Cleveland Meeting of the American Physical Society.

<sup>4</sup> Fuson, *THIS JOURNAL*, **46**, 2779 (1924); **47**, 2018 (1925).

<sup>5</sup> Hassel and Mark, *Z. Physik*, **25**, 317 (1924); Bernal, *Proc. Roy. Soc. (London)*, **A106**, 749 (1924).

<sup>6</sup> Lonsdale, *Proc. Roy. Soc. (London)*, **A123**, 494 (1929).

<sup>7</sup> Pauling, *Phys. Rev.*, **36**, 430 (1930).

produce the type of oscillation suggested. At sufficiently low temperatures this oscillation should cease. One would expect, therefore, small "humps" in the heat capacity curves of all benzene derivatives (unless oscillation is prevented by external forces), similar to those found<sup>8</sup> for certain of them which have been attributed<sup>7</sup> to rotation of  $\text{CH}_3$  groups.

Another alternative is to assume easy (not necessarily frequent) oscillation and that the orientation of the puckering in a particular molecule in crystalline  $\text{C}(\text{CH}_3)_6$  does not depend on the orientations in surrounding molecules.

The "anomalous" isomerism found among biphenyl derivatives may perhaps be due to non-oscillating puckered rings, rather than to a lack of free rotation about the bond joining them.

X-Ray studies have revealed no cases of two mutually perpendicular planes of symmetry passing through benzene ring centers (as would be expected if the rings were plane), although in several cases a center of symmetry has been found.<sup>9</sup> X-Ray evidence also definitely favors models with equivalent atoms at or oscillating about the corners of a regular hexagon. A satisfactory model must account, moreover, for the synthesis of benzene derivatives, first by methods indicating 1,4-linkages and second, by simple ring closure of a conjugated system.<sup>10</sup> The writer knows of no model, other than that proposed here, which meets these requirements.

From this model one would predict that "electron density" calculations from accurate x-ray intensity data by the method of Fourier Series summations<sup>11</sup> would show the carbon atom "peaks" to be considerably elongated normal to the "plane of the ring."

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#### GRADUAL TRANSITION IN CRYSTALLINE SODIUM NITRATE<sup>1</sup>

*Sir:*

Some interest has been elicited in recent years in gradual transitions in crystalline solids. In these transitions the heat capacity of the crystal alters abnormally over an extended range of temperatures, with a more or less well-defined temperature at which the heat capacity reaches a maxi-

<sup>8</sup> Huffman, Parks and Daniels, *THIS JOURNAL*, **52**, 1547 (1930).

<sup>9</sup> See, for instance, Hendricks, *Chem. Rev.*, **7**, 431 (1930).

<sup>10</sup> Ingold, *J. Chem. Soc.*, **121**, 1143 (1922).

<sup>11</sup> Duane, *Proc. Nat. Acad. Sci.*, **11**, 489 (1925); Havighurst, *ibid.*, **11**, 502 (1925); Compton, "X-Rays and Electrons," D. Van Nostrand Co., Inc., New York, 1926, p. 151; W. L. Bragg, *Proc. Roy. Soc. (London)*, **A123**, 537 (1929).

<sup>1</sup> Abstract of a presentation made at the February meeting of the Washington Section of the American Chemical Society, Washington, D. C.