

in this material. The amount of α -ray radiation required to produce a reversed halo must be very much greater than this, as is shown by Jedrzejowski's³ work on the production of reversal by α -ray radiation of a Siberian mica. Thus if we are to assume that hibernium halos are due to samarium, we must either conclude that Ytterby mica is specially sensitive to α -ray radiation, or that some reversal and intensification of the halos has been produced by either thermal or chemical effects in the course of their long history. I am inclined to favour the latter alternative, since I have observed a similar intensification of positive halos when heated to a temperature not sufficient to obliterate the halo by the blackening of the surrounding mica⁴. Joly, also, has observed the reversal of immature uranium halos in Ytterby mica. The fact that hibernium halos are so rare, even in Ytterby mica, is perhaps explicable on the view that the conditions for the reversal and intensification of the halos are only very occasionally satisfied.

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March 29.

¹ *Proc. Roy. Soc., A*, **102**, 682; 1923.

² *Phil. Mag.*, p. 644, April 1913.

³ *C.R.*, **186**, 135; 1928.

⁴ *Phil. Mag.*, p. 132, Jan. 1928.

Volumes of Alkyl Groups and their Orienting Powers

In some of their applications, the current generalised theories of benzene substitution discard steric factors too lightly. For the purpose of *a priori* consideration, it can be assumed that the effective reagent in a substitution does not occupy a *smaller* volume than the group which is eventually installed in place of hydrogen.

A drawing to scale¹ is reproduced (Fig. 1) of the compound (i): the groups R_1 and R_2 are omitted and the two positions which could be taken by the methyl group in the plane of the benzene ring are indicated.

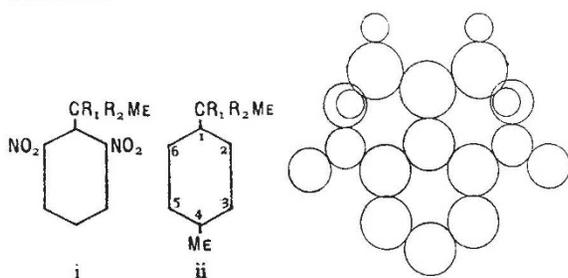


FIG. 1. Scale drawing of (i)

It is seen that some degree of interlocking of groups occurs. Various applications of this are at present under investigation; for example, that during nitration of (ii), attack by HNO_3 molecules at the 2- and 6- positions might be impeded by a real screening effect from the $-\text{CR}_1\text{R}_2\text{Alk}$ radical. To a less extent the same might apply to halogenation. Thus the absolute number of reagent molecules colliding with these positions may be less than those colliding at 3- and 5-, and/or some of the reagent molecules may succeed in penetrating to the 2:6-carbon atoms only after preliminary collision. In the last case, their kinetic energies being reduced,

the threshold energy of activation necessary for substitution is likely to be attained less frequently than among the more direct collisions occurring at positions 3- and 5.

Expressed differently: if velocities of substitution can be represented by $k = \alpha e^{-E/RT}$, then in compounds of the type now under discussion the two pairs of vicinal positions available for substitution will be abnormal in not having identical α terms (contrast Bradfield and Jones's results²). Such abnormality must be expected with all alkyl substituents larger than methyl.

The net consequence will be a depression of substitution ortho to the radical, $-\text{CR}_1\text{R}_2\text{Alk}$ in favour of other positions where substitution will be able to occur by default. Thus orientation in discord with electronic theories (requiring substitution more at positions of greater electron availability) should be expected from *a priori* reasoning alone.

Experiments on the nitration and halogenation of *p*-cymene and some of its derivatives have justified this conclusion. The results with the hydrocarbon itself are tabulated:

268 G <i>p</i> -cymene subjected to:—	2-Substitution in 1-methyl-4-isopropylbenzene.					
	Total wt. of crude material isolated	Unchanged <i>p</i> -cymene recovered	Theoret. yield for mono substn.	Pure 2 subst. cymene obtd.	Per cent in crude product.	Per cent yield on cymene taken
Nitration	290	—	358	252	87	70
Chlorination	318	1	338	200	63	59
Bromination	376	19	396	214	57	54

The numbers in the last column give minimum estimates of the yields of 2-derivatives obtained in these experiments. The amount of actual 2-substitution of *p*-cymene in each case is certainly greater than is indicated by these results. Thus methyl appears to possess a greater ortho directive influence than isopropyl. On pure electronic theories the reverse should be the case.

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¹ "Atomic Radii", *An. Rep. Chem. Soc.*, p. 402; 1931.

² Bradfield and Jones, *J. Chem. Soc.*, 1009; 1928.

Nuclear Moment of Arsenic

THE hyperfine structure of two-electron spectra of heavy elements with configurations involving an *s* and one other type electron have been under investigation for some time in this laboratory. The As IV spectrum, classified by K. R. Rao¹, is of this type, and is particularly suited for the detection of hyperfine structure and the determination of the moment of the nucleus. About a year ago, the As IV lines $\lambda 3216, 3190, 3109$ ($4s5s^3S_1 - 4s5p^3P_{0,1,2}^o$), excited by a condensed electrodeless discharge, were examined with a multiple prism spectrograph and found to have comparatively large hyperfine structures. The patterns, although not completely resolved, showed that the *I* value of arsenic was small and probably equal to $1\frac{1}{2}$. The recent acquisition by this Department of an excellent 21 ft. concave grating, ruled by Prof. Gale of Chicago, has made possible the completion of this investigation. The results definitely show that the nuclear moment of arsenic is $1\frac{1}{2} \times h/2\pi$.