Configurations of Arenechromium Tricarbonyls

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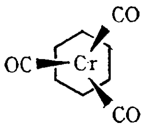
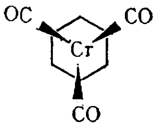
IN the solid state benzenechromium tricarbonyl[1] and hexamethylbenzenechromium tricarbonyl[2] display the staggered molecular configuration (I). Anisolechromium tricarbonyl, on the other hand, adopts the eclipsed configuration (II).[3] If the bonding of the chromium atom is described in terms of octahedrally-directed localized σ-orbitals, then the three metal orbitals directed towards the benzene ring of anisolechromium tricarbonyl point at the carbon atoms *ortho* and *para* to the methoxyl substituent.[3] We favoured the view that this configuration is a manifestation of the electron-releasing *o,p*-directing character of a methoxyl substituent on a benzene ring, but recognized that crystal-packing forces and/or intramolecular van der Waals attractive forces between the methoxyl group and the nearest carbonyl group might play a role.



(I)



(II)

To provide more information about the relative

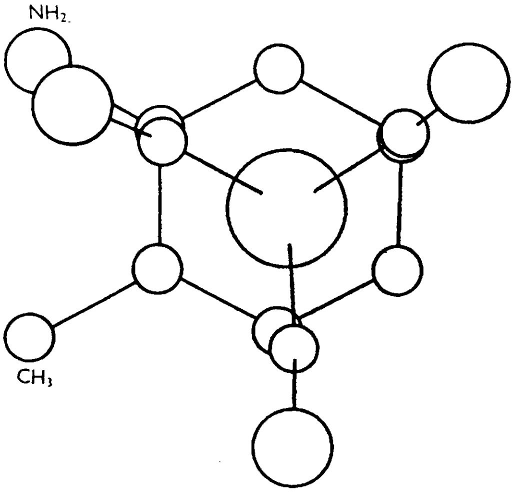


FIGURE: *The arrangement of atoms in a molecule of* o-*toluidinechromium tricarbonyl as viewed in projection on to the plane of the benzene ring.*

contributions of these factors we have now determined the crystal structure of *o*-toluidinechromium tricarbonyl. The crystals are monoclinic, space group *C*2/*c*, with eight molecules of $C_{10}H_9NO_3Cr$ in a cell of dimensions $a = 19{\cdot}25$, $b = 8{\cdot}32$, $c = 13{\cdot}80$Å, $\beta = 107^\circ\,0'$. After Fourier and least-squares refinement of the atomic parameters the value of *R* is now 14·4% over 1448 independent reflexions. Our results, which are summarized in the Figure, establish that in this molecule the carbonyl–chromium vectors point closely towards the benzene carbon atoms which are *ortho* and *para* to the NH_2 substituent. (The NH_2 and CH_3 groups were distinguished on the basis of peak heights, bond lengths, and the participation of the NH_2 group in hydrogen bonding with oxygen atoms of neighbouring molecules.) We conclude that the configurations of substituted benzenechromium tricarbonyls directly reflect the electron-releasing or electron-withdrawing character of the substituents on the aromatic rings, and are not influenced to any appreciable extent by non-bonded interactions.

(*Received, February* 21*st*, 1966; *Com.* 113.)

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[2] M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, 1965, **4**, 1298.

[3] G. Huttner, E. O. Fischer, R. D. Fischer, O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Organometallic Chem.*, 1966, in the press.