

06.2-13 BONDING AND LONE-PAIR DENSITY IN TETRAFLUOROTEREPHTHALONITRILE, $C_6F_4(CN)_2$. By J. D. Dunitz, W. B. Schweizer and P. Seiler, Laboratorium für Organische Chemie, ETH-Zentrum, CH-8092 Zürich, Switzerland.

The crystal structure of tetrafluoroterephthalonitrile $C_6F_4(CN)_2$ has been determined at room temperature by van Rij and Britton (Cryst. Struct. Comm. 10, 1981) who pointed out that this compound (space group $Cmca$, $Z = 4$, molecular symmetry $2/m$) is an excellent candidate for a careful bonding-density study at low temperature.

We have measured two data sets at 98 K; a "normal" set extending to $\sin\theta/\lambda = 0.8 \text{ \AA}^{-1}$, b) a more accurate (8 equivalent reflexions) and more extensive set extending to $\sin\theta/\lambda = 1.15 \text{ \AA}^{-1}$. For set (a) we used exponentially modified weights (Dunitz and Seiler, Acta Cryst. A29, 589, 1973) with $r = 5 \text{ \AA}^2$; for set (b) we tried several weighting systems and finally chose $\omega = (\omega_{\text{obs}} e^{as^2}) / (b + e^{as^2})$ with $b = 2 \times 10^4$, $a = 36 \text{ \AA}^2$, an expression which gives effectively constant weight to reflections with $s > 0.6 \text{ \AA}^{-1}$ but without the discontinuity introduced in conventional high-order refinement based on a step-function. Bond distances derived from the two independent data sets agree within 0.003 Å, U^j values within 0.0013 Å². Difference X-X maps show clearly defined bonding density for all bonds except the highly polar C-F bond, which is almost featureless for both data sets. The map for set (b) shows a well defined lone-pair density at N as well as extremely diffuse density around the F atom.

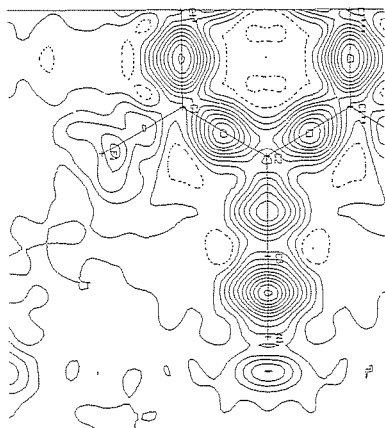


Figure X-X density in molecular plane. Contours at intervals of $0.075 e \cdot \text{Å}^{-3}$.

The contrast between the well defined bonding density in homopolar C-C bonds and the relative absence of bonding density in the C-F bond is striking.

06.2-14 ANALYSIS OF NET ATOMIC CHARGES IN TRANSITION METAL CARBONYLS BY A POLYHEDRAL SPACE PARTITIONING TECHNIQUE.* By A. Holladay, P. Leung, G. Moss & P. Coppens, Chemistry Department, State University of New York at Buffalo, Buffalo, New York 14214

A space partitioning algorithm based on space-filling polyhedral volumes surrounding each atom (P. Coppens & T. N. Guru Row, Ann. N.Y. Acad. of Science (1978) 313, 244) has been applied to a number of transition-metal carbonyl complexes. The average electron density per unit volume at the surface of the polyhedron is given by dQ/dV , where dQ is the change in the integrated total electron density upon increasing polyhedron size and dV is the associated increase in volume. dQ/dV shows a minimum as a function of the position of the polyhedron boundary which is located about halfway between the transition metal and the adjacent carbon atom. The corresponding definition of atomic volume leads to a negative charge of about 0.4 electrons on each of the cobalt atoms in $Co_3(CO)_9CH$ when integration is performed on the deformation density, but a charge of about +1 electrons when the total observed density is integrated. The difference is even more pronounced for $Cr(CO)_6$ for which charges of -0.4 and +4.0 are obtained for integration on $\Delta\rho$ and ρ_{obs} respectively. The discrepancy can be understood by examination of integration results on isolated Co and Cr atoms which show most of the 4s and part of the 3d electron density to be outside the defined volume of integration.

Since the bonded atom is more negative than the spherical atom in the promolecule the conclusion is reached that the transition metal atoms investigated are slightly negative. The results are in general agreement with net charges obtained with the kappa refinement least squares technique which uses a quite different definition of the atomic volume.

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06.2-15 AN ELECTRON-DENSITY STUDY OF TiC. By A. Dunand, H.D. Flack and K. Yvon, Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24, quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland.

Titanium monocarbide is a hard, brittle, refractory metallic solid ($T_m \sim 3200^\circ\text{C}$) which has the NaCl type structure. In order to study its bonding, deformation density maps were calculated from experimentally measured X-ray intensities of a nearly spherical single crystal ($\bar{r} = 84(2) \mu\text{m}$) of composition $TiC_{0.940(5)}$ * ($a = 4.3295(1) \text{ \AA}$, 1464 reflexions with $\sin\theta/\lambda \leq 1.31 \text{ \AA}^{-1}$, Nb filtered MoK_α radiation, ω - 2θ step scans, 0.01°s^{-1}).

After averaging symmetry equivalent reflexions (internal consistency $R = 0.012$) a set of 59 unique reflexions was obtained. A least-squares refinement of the scale factor (k), two temperature factors ($U(Ti)$, $U(C)$), one occupancy factor ($p(C)$) and an isotropic type extinction parameter (g) using scattering factors of neutral atoms and including all observed reflexions gave an agreement index $R_w = 0.007$ ($GoF = 6.7$).

The parameters obtained are $U(Ti) = 0.00324(4) \text{ \AA}^2$, $U(C) = 0.0030(2)$, $p(C) = 0.91(1)$, $g = 39(1)$, $\sigma(k)/k = 0.005$. The correlation coefficients greater than 0.5 are $c(k, g) = 0.90$, $c(k, U(Ti)) = 0.95$, $c(g, U(Ti)) = 0.81$ and $c(p(C), U(C)) = 0.92$.

A high-order refinement ($0.60 \leq \sin\theta/\lambda \leq 1.31$) did not produce significantly different results.

The deformation density map shown in Fig. 1 was calculated from high order data only ($\sin\theta/\lambda > 0.6 \text{ \AA}^{-1}$). Clearly, the 3d contribution to the scattering persists at large Bragg angles, revealing sharp bonding features of e_g symmetry around the Ti atom sites. These are con-