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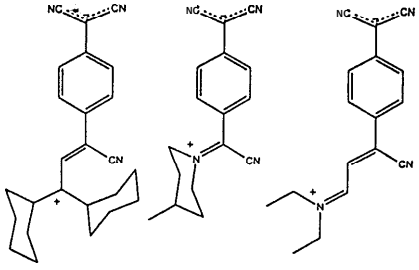
Report: It has been found that a deeper understanding of the nature of (a) charge transfer processes and (b) intermolecular forces in non-linear optical (NLO) materials is the key to the optimization of the second-harmonic generation (SHG) effect. In light of these findings, we have been studying the structure / property relationships in various SHG-active organic materials[1-3]. Such work has included performing very accurate charge density studies[3,4] since these provide an ideal route to improved understanding in both areas (a) and (b). We are especially interested in a novel class of zwitterionic tetracyanoquinodimethane (TCNQ) derivatives for which the scalar product, $[\mu.\beta]$ is exceptionally large[5] and the optical absorbance not only occurs at very low wavelengths but is also very sharp, thus giving rise to potential applications as 'optical windows' [6]. Therefore, three of these materials, (Scheme 1) were the subject of this investigation.

Several crystals of each compound were tried. However, crystals of compounds A and B diffracted too weakly to justify attempting a charge density study even for crystals with dimensions equal to the maximum physically permitted. A crystal of compound C diffracted strongly enough out to a high value in $\sin\theta/\lambda$ (λ = 0.24881). Therefore, a charge density data collection was performed on C following a strategy which resulted in the collection of 80% of all unique reflections out to a resolution of $0.5 Å^{-1}$ and with an average redundancy of 1.3.



A B C

Scheme 1: The three TCNQ derivatives studied in this experiment.

During data collection ice constantly built-up on the crystal due to a poorly performing zeolite in the air flow of the cryostream. Therefore, the ice had to be carefully removed at regular intervals. Shortly before the scheduled end of the data collection, the crystal was unfortunately disloged from its position during one of the attempts to remove the obstructing ice. Hence, the data collection was terminated slightly early. Despite this misfortune, the amount of data that had already been collected seemed to be sufficient for our needs.

As a result of the events described above, we were left with sufficient time to perform a charge density data collection on an organic NLO material from another series which we were investigating. Data collection on a crystal of this compound, 4-aminobenzophenone, (ABP) was performed using a strategy which yielded 97% unique reciprocal-space coverage out to a resolution of $0.5 Å^{-1}$ and with an average redundancy of 3.0. Data collection proceded without any problems.

Subsequent data reduction showed that the data of compound C was of good quality but that of ABP was not since more rigid indexing showed it to be slightly twinned. There also appeared to be a problem with the scaling procedure since on merging the data, the residual factor was anomalously high - i.e. > 10%. Further investigations have shown that without correcting this problem, the data will not be usable for a charge density study. In order to overcome this problem, we are in the final stages of writing a new scaling program which uses a completely empirical approach to correct the data unlike the default program which relies on symmetry equivalents to scale the data suitably. If the new program accomplishes its required task, then we will attempt to perform a full multipolar charge density analysis of C.

References

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