

SHORT COMMUNICATIONS

INTERPRETATION OF THE REFRACTIVE AND ROTARY DISPERSION OF CRYSTALLINE LiIO_3

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LITHIUM iodate (LiIO_3) belongs to the pyramidal class 6 of the hexagonal system, with space group $\text{P6}_3^{1,2}$ exhibiting high optical activity³. Because of their very good optical quality, these crystals have been of considerable interest.

Umegaki *et al*⁴ have measured the refractive indices for both the ordinary (n_o) and extraordinary (n_e) rays in the spectral range $0.4047\ \mu$ to $2.2493\ \mu$ to an accuracy of ± 0.0001 in the visible region and ± 0.0003 in the near infrared region. It is well known that the refractive dispersion can be explained by the Sellmeier-Drude (S-D) type formula. We have fitted the experimental data using the three-term S D formulae,

$$(n_o - 1)^2 = \frac{2.0604 \lambda^2}{\lambda^2 - (0.12)^2} + \frac{0.3536 \lambda^2}{\lambda^2 - (0.23)^2} - 0.00816 \lambda^2 \quad (1)$$

and

$$(n_e - 1)^2 = \frac{1.7240 \lambda^2}{\lambda^2 - (0.12)^2} + \frac{0.1915 \lambda^2}{\lambda^2 - (0.23)^2} - 0.00376 \lambda^2 \quad (2)$$

The first two terms in the above equations represent the contributions from the deep and near ultraviolet bands and the third term represents the contributions from the infrared bands which are lumped together. The absorption wavelengths $0.12\ \mu$ and $0.23\ \mu$ account for the dispersions of both n_o and n_e satisfactorily, but with different oscillator strengths. (Our attempts to fit the experimental data with either a single term or a two-term formula did not yield satisfactory results). The near ultraviolet absorption band *viz.*, $0.23\ \mu$ is close to the experimentally observed band with a peak at $0.253\ \mu$ ⁵. Regarding the use of deep ultraviolet band at $0.12\ \mu$, it may be pointed out that the rotatory and refractive dispersion of $(\text{AlIO}_3)_3 \cdot 2\text{HIO}_3 \cdot 6\text{H}_2\text{O}$ have been explained well using a two-term quadratic formula assuming absorption bands around $0.1\ \mu$ and $0.2\ \mu$ ⁶.

We have therefore attempted to verify whether the same absorption wavelengths can also be used to

explain the dispersion of rotatory power using different types of formulae^{7,8}. A two-term Drude type equation

$$\rho = - \frac{2.1300}{\lambda^2 - (0.12)^2} + \frac{31.1300}{\lambda^2 - (0.23)^2} \quad (3)$$

is found to give a good fit with the experimental data³ to a reasonable accuracy.

Using a two-term Chandrasekhar type equation

$$\rho = \frac{24.6783 \lambda^2}{[\lambda^2 - (0.16)^2]^2} + \frac{4.1877 \lambda^2}{[\lambda^2 - (0.23)^2]^2}, \quad (4)$$

the agreement between the calculated and the experimental data is still better; however, the deep ultraviolet band at $0.16\ \mu$ appears to be ambiguous.

There have already been a few attempts to explain the rotatory dispersion of LiIO_3 . The first attempt was made by Janku and Vysin⁹, by the graphical method using the Born-Vysin relation, but this did not explain the dispersion throughout the spectral range. Subsequently Perekalina *et al*⁵ tried (i) a single term Drude type equation

$$\rho = \frac{29.4}{\lambda^2 - (0.232)^2} \quad (5)$$

and (ii) the improvised Born-Vysin equation

$$\rho = \frac{29.9}{\lambda^2 - (0.234)^2} - \frac{0.6 \lambda^2}{[\lambda^2 - (0.234)^2]^2} \quad (6)$$

We find that equations (5) and (6) give a better fit than the equation proposed by Janku and Vysin⁹ and the absorption wavelengths used in these equations are close to the experimentally observed absorption band. In all these computations, we used the TDC-316 Computer (ECIL, India) and adopted the least square technique. We have restricted the computations to the spectral range 0.286 to $0.628\ \mu$ since the extended experimental data for the region $0.628\ \mu$ to $0.925\ \mu$, stated to have been measured by Perekalina *et al*⁵ are not available.

The sum of the squares of deviations $\delta = \sum (\rho_{\text{exp}} - \rho_{\text{cal}})^2$ from (3), (4), (5) and (6) works out to be 603, 536, 676 and 860 respectively and the standard error, $(\delta/n)^{1/2}$, where n is the number of experimental points, are respectively 4.82, 4.54, 5.10 and 5.75. It should be mentioned that δ for (5) and (6) is significantly different from the values 607 and 608 respectively, as reported by Perekalina *et al*⁵. Although the quadratic type formula (4) gives the best fit, as already

stated, the use of the absorption band at 0.16μ appears to be ambiguous.

The Drude-type formula characterises the optical activity as arising due to an asymmetric structure of the molecule. The analysis carried out by Perekalina *et al*⁶ shows that the crystal structure of LiIO_3 does not possess a screw character but only an asymmetrization of IO_3^- which leads to its optical activity.

Since the same absorption wavelengths, viz. 0.12 and 0.23μ , account for the refractive dispersion (1) and (2) and also the rotatory dispersion (3) it can be concluded that the Drude-type formula is probably more appropriate for explaining the rotatory dispersion of this crystal.

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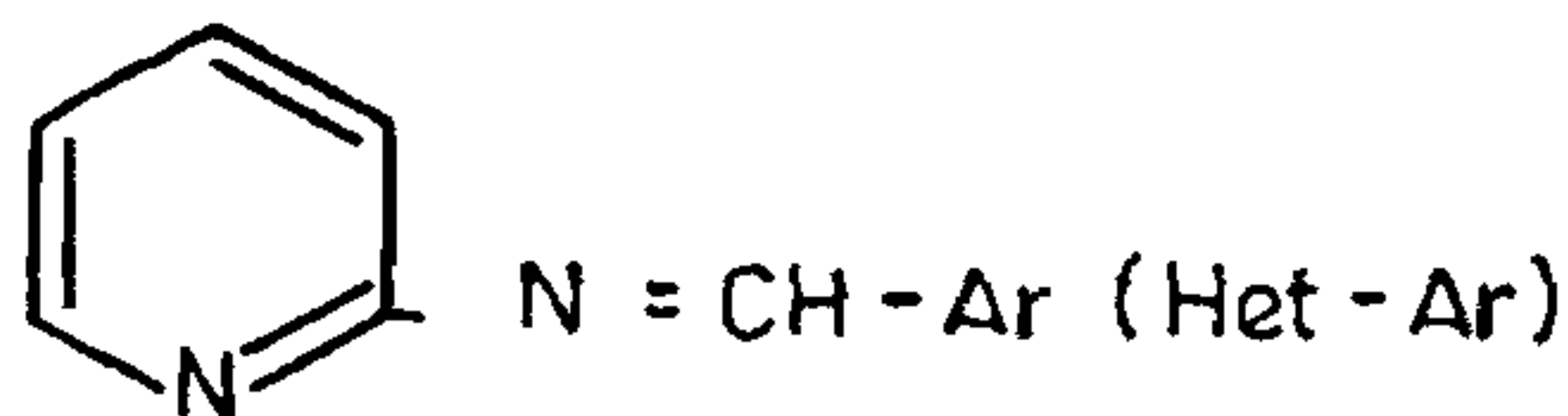
SYNTHESIS OF SOME NEW N-OXIDOPYRIDYLTHIAZOLIDIN-4-ONES

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DIVERSE biological activities have been found to be associated with 4-thiazolidinone derivatives¹. The

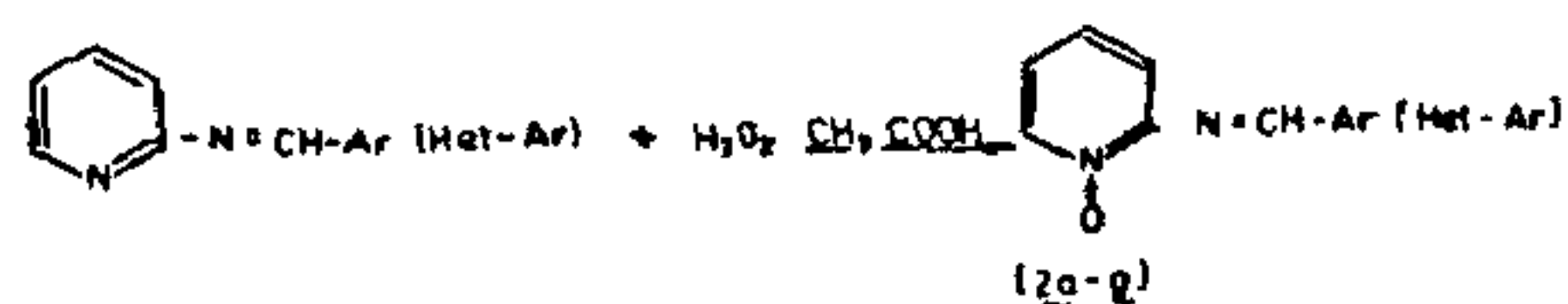
chemotherapeutic efficiency of these compounds as local anesthetic and anticonvulsant agents^{2,3}, is of interest and justifies a detailed study of the toxicological properties of the most active compounds. As part of our studies on the chemistry of thiazolidinone heterocyclic systems⁴⁻⁹ it is of interest to incorporate a polar function into the moiety of such molecules. Since it has been reported that N-oxide heterocyclic compounds are more polar and with much lower partition coefficient values which make them interesting for studying pharmacological properties¹⁰ we describe here the synthesis of N-oxidopyridylthiazolidin-4-ones by (i) preparing the key intermediates, aryl-(heteroaryl)-idene-2-aminopyridine-N-oxides (2a-h) and (ii) cyclocondensation of the key intermediates on mercaptoacetic acid.

Aryl-(heteroaryl)-idene-2-aminopyridines were obtained by the condensation of 2-aminopyridine with different aldehydes in ethanol using piperidine or piperidine acetate as a basic catalyst.

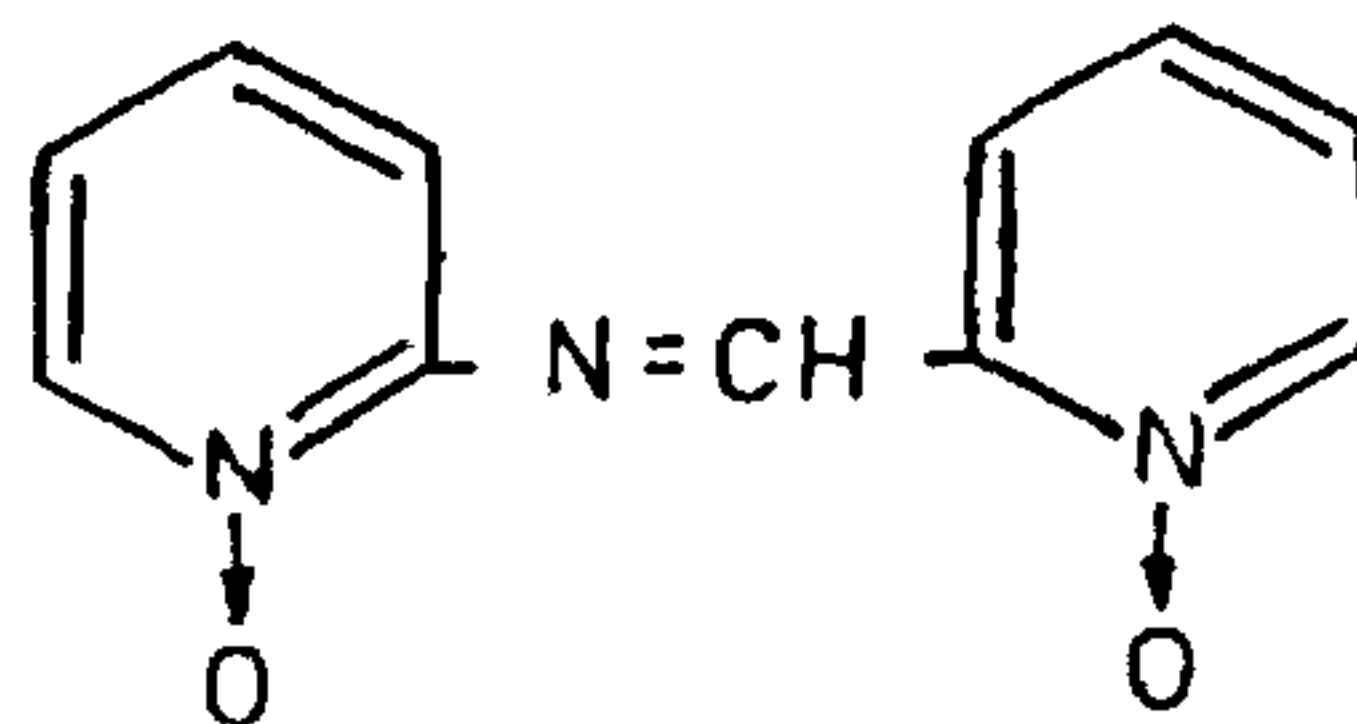


- lg - h
- | | |
|---|--|
| 1a, Ar C_6H_5- | b, Ar $p\text{-Cl-C}_6\text{H}_4-$ |
| c, Ar $o\text{-OH-C}_6\text{H}_4-$ | d, Ar $p\text{-OH-C}_6\text{H}_4-$ |
| e, Ar $p\text{-NO}_2\text{-C}_6\text{H}_4-$ | f, Ar $p\text{-N(CH}_3)_2\text{-C}_6\text{H}_4-$ |
| g, Heteroaryl thienyl | h, Heteroaryl pyridyl |

N-oxidation of these derivatives was achieved by interaction with hydrogen peroxide in glacial acetic acid.



in the case of compound 1h the reaction afforded the corresponding dioxide (2h).



The structure of the compounds (2a-h) was established both by microanalytical as well as spectral data. Infrared spectra show strong absorption bands in $1260\text{-}1320\text{ cm}^{-1}$ region due to $\text{N} \rightarrow \text{O}$ as well as defined bands in the region $1640\text{-}1580\text{ cm}^{-1}$ due to $\nu \text{C} = \text{N}$.