Dynamic orientational disorder of the nitro group in 2-chloro-nitrobenzene revealed through ^{35}Cl nuclear quadrupole resonance

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Abstract
In the present paper we analyse the contributions of nitro group movements in
2-chloro-nitrobenzene to the nuclear quadrupole resonance (NQR) parameters
of the chlorine nucleus in the molecule. We found two contributions to the
spin–lattice relaxation time (T_1) and the NQR frequency (ν_Q) due to the onset
of nitro group movements in the molecule. One of these contributions is the
well-known semirotation of the nitro group around the N–C axis. The other
one is attributed to some tilting or tipping of the nitro plane away from the
benzene ring introducing some dynamic orientational disorder of this group in
the crystal only observed as a contribution from the temperature dependence of
T_1 and ν_Q. Its activation energy is similar to that of the nitro group reorientation
(21.9 and 23.6 kJ mol^{-1} for the two processes) and may arise from competing
crystalline and steric chlorine nucleus effects. The present investigation shows
that in chloronitrobenzenes the NO$_2$ group dynamic orientational disorder can
produce modulation effects on the chlorine T_1 which are large enough to be
observed by means of the NQR.

1. Introduction

The experimental search for new organic material properties desirable for non-linear optical
processors has led to the study of the large polarizability of nitrobenzene and also the linkage
of a π-electron to a nitro group in the molecule. The aim of this paper is to study the dynamics
of the NO$_2$ group when it is bound to an aromatic ring through the analysis of the nuclear
quadrupole resonance (NQR) of a ^{35}Cl nucleus near the nitro group in the molecule. Thus,
our study will be focused on the NQR of chlorine in chloronitrobenzenes.

The very high sensitivity of a quadrupolar nucleus to change in its environment as well as the dynamics of molecule motions in molecular crystals is well known [1, 2]. The NQR provides valuable information on the motional dynamics of either a whole molecule or its fragments. The nitro group modifies the electric field gradient, EFG, at the site of the chlorine nucleus by changing the ^{35}Cl NQR frequency, ν_Q, considerably. This alteration is strongest when the NO_2 group substitutes for the ortho-position hydrogen; here ν_Q increases by around 8% from that of chlorobenzene. This increment is only 2.5% if one substitutes for the meta-hydrogen. Substitution for the *para*-hydrogen left the ν_Q almost unchanged (the change was only 0.7%, probably due to crystalline packing effects). Also, the movement of a molecular group close to the chlorine nucleus introduces some fluctuations in its EFG contribution which makes a strong contribution to the spin–lattice relaxation times.

Our study is made on 2-chloro-nitrobenzene. These molecular solids, unlike the 4-chloro-nitrobenzene previously studied in our laboratory, have a strong and sharp NQR signal (linewidth between 4 and 7 kHz); that is a sign that no crystalline structure disorder is present, as in the case of *para*-chloro-nitrobenzene. This allows us to perform a comprehensive analysis of the NO_2 group effects on the NQR of a nearby ^{35}Cl nucleus.

In our experiment we found that besides the well-known semirotation of the NO_2 group around the N–C axis, this molecular group also shows dynamic disorder at temperatures higher than 230 K, as evidenced by its effect on the ^{35}Cl NQR. The focus of our study is related to the identification of this dominant relaxation process at high temperatures ($T > 230$ K). This dynamical disorder may arise from movements of the NO_2 group out of the aromatic ring, with activation energy and a correlation time similar to those of the semirotation of this molecular group. Such a narrow range of values of the activation energies, 21.9 and 23.6 kJ mol^{-1}, prevent us from assigning these contributions to T_1 and ν_Q.

In this paper we use an extension of the Seliger model [3] to analyse the effects on nuclei subjected to a perturbation Hamiltonian $H(t)$ that randomly exchanges between different H_i-values.

2. Experimental details

Polycrystalline samples of 2-chloro-nitrobenzene were obtained commercially, and purified by successive recrystallizations before being sealed in glass containers to avoid hydration of the sample. After these recrystallizations we observed that the melting point of the sample ranged within 1 K.

The sample was cooled down at a very slow rate up to a temperature close to 80 K and then kept at around 48 h before the beginning of the experiment. We took a reading of NQR parameters every 5 K approximately within the 80–180 K regions and within the 230 K to the room temperature region. In the 180–230 K region the reading was made every 2 K for better observation of the effects due to the onset of the NO_2 group reorientation. All changes in sample temperature were achieved in the slowest possible way to prevent the occurrence of internal strain in the sample that might diminish the signal-to-noise ratio. The temperature of the sample was kept constant to within 0.1 K during the measurement. The probe-head was placed inside a temperature-controlled thermal bath. A home-made temperature control device, covering the range 80–400 K, consisting of four coaxial and partially insulated (with aluminium oxide powder) copper cylinders immersed in a liquid N_2 bath, was used. The temperature control was effectively achieved by heating an inner cylinder with an electronically driven heater. The temperature control was achieved with a copper–constantan thermocouple and an Eurotherm 2604 controller.
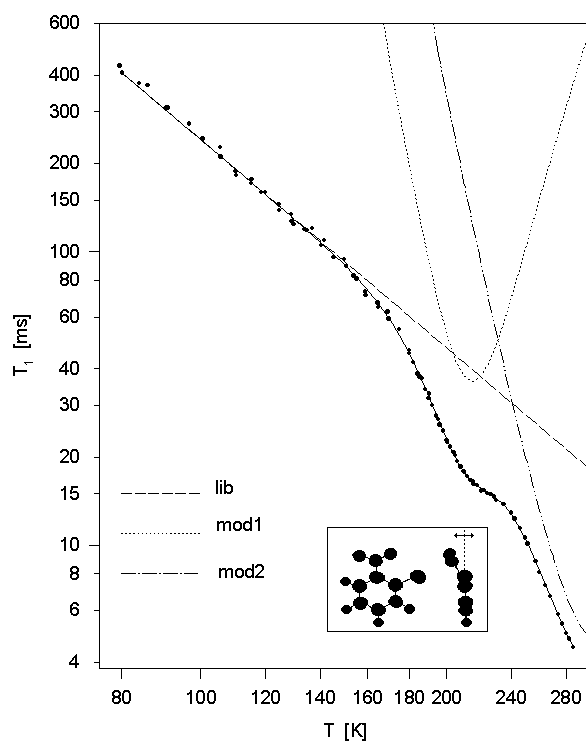
Figure 1. A log–log graph showing the temperature dependence of the spin–lattice relaxation times T_1. The solid curve represents the fit of the $T_1(T)$ data with equation (12) containing one librational power law and two EFG modulation contributions arising from semirotation and orientational disordering of the NO_2 group. The inset is a diagram of the molecule 2-chloro-nitrobenzene showing schematically the nitro group tipping or tilting away from the plane of the aromatic ring, as suggested by Abdel-Halim *et al* [8].

We used a pulsed, broadband, fully computer-controlled, home-made NQR spectrometer equipped with a HP8656B frequency synthesizer, an AR 150LA transmitter, a MATEC 625 receiver with a MATEC 253 preamplifier. Data acquisition was achieved with a WaagII data acquisition ISA Board from Markenrich. The control and automatic measurement computer program was developed in our laboratory.

The ν_Q-values were obtained within 100 Hz by fitting the FFT of the FID and looking for its maximum; PEAKFIT V4 software was used to find the central frequency and the linewidth. T_1-values were determined within 5% by fitting around 25 data points of the relaxation function $S(\tau)$ in a $\pi/2$–τ–$\pi/2$ two-pulse sequence as follows: 20 data points with a pulse interval τ from 0.1 to $3T_1$, and then 5 or 6 more points in the $3T_1$-to-$10T_1$ interval. The thermal stability of the samples was controlled by checking that there were no changes in the value $S(10T_1)$ during the measurements; all 'bad' readings where this value changed during the measurement interval were discarded.

3. Results

3.1. Spin–lattice relaxation time

Figure 1 shows the temperature dependence of T_1 for the 2-chloro-nitrobenzene over the whole range of measurements (80–300 K). $T_1(T)$ reveals certain mechanisms of nuclear relaxation

that are effective in different ranges of temperature inside the region from 80 to 300 K. At low temperatures, $T < 165$ K, the general behaviour of $T_1(T)$ follows the well-known power law arising from molecular librations [1]:

$$T_1^{-1}|_{lib} = aT^\lambda \tag{1}$$

with $a = 2 \times 10^{-5}$ s K^{-1} and $\lambda = 2.6$. There is a departure from the librational behaviour near 200 K, indicating contributions to T_1 due to the onset of the NO$_2$ semirotation. These semirotations modulate the EFG at the chlorine nucleus site, giving us an additional contribution to the spin–lattice relaxation time. The contribution to the spin–lattice relaxation time predicted by the Woessner and Gutowsky model [4] is

$$T_1^{-1}|_{mod} = \frac{1}{3}\left(\frac{q'}{q}\right)^2 \frac{\omega_Q^2 \tau_c}{1 + \omega_Q^2 \tau_c^2} \tag{2}$$

with the correlation time $\tau_c = \tau_0 \exp(U/RT)$ and U is the activation energy for the reorientation of the nitro group thorough a 180° jump; (q'/q) is the ratio between the modulated fraction of the EFG and its principal component.

Both librational and nitro group semirotation contribute to the spin–lattice relaxation and are considered as independent processes; thus,

$$T_1^{-1} = T_1^{-1}|_{lib} + T_1^{-1}|_{mod} \tag{3}$$

must fit our $T_1(T)$ data. This expression has a qualitative similarity with data for temperatures below 230 K. Indeed, the best-fit parameters obtained by fitting the data in the 80–230 K region are

$$U = 18.3 \text{ kJ mol}^{-1} \qquad \tau_0 = 2.3 \times 10^{-13} \text{ s} \qquad (q'/q) = 1.3 \times 10^{-3}.$$

The data follow this trend for $T \leqslant 230$ K but disagree in the high-temperature region. That is, molecular librations and nitro group semirotation *per se* cannot account for our experimental data. Instead, we must think of an additional contribution to the relaxation processes dominant at high temperatures.

We made an attempt to fit the $T_1(T)$ data by assuming a relaxation contribution from a reorientation of the whole molecule. Alexander and Tzalmona's theory [5] predicts a temperature dependence for T_1 given by

$$T_1^{-1}|_{reo} \approx \frac{1}{\tau_r} e^{-\frac{E_a}{kT}} \tag{4}$$

where E_a is the activation energy for such molecular reorientation.

Then, we must add this expression to equation (3) to fit all the T_1-data of figure 1. The best-fit parameters obtained by a least-squares fit with the expression

$$T_1^{-1} = T_1^{-1}|_{lib} + T_1^{-1}|_{sr} + T_1^{-1}|_{reo} \tag{5}$$

make a slight modification to the librational and modulation parameters. For the reorientation parameters, while the E_a-value obtained is reasonable, the value for τ_r is too large; thus we obtain $\tau_r = 2 \times 10^{-6}$ s while the expected value is $\tau_r \approx 10^{-13}$ s for realistically representing the limiting lifetime for a reorientation of the whole molecule. The extremely large fitted value is meaningless; even when this model provides a temperature dependence function that can be fitted to data, the parameters obtained are not acceptable. Any contribution to the nuclear relaxation based on whole-molecule semirotations must be excluded because it leads to unrealistic values of τ_r or the activation energy for this process. An attempt to explain this T_1-behaviour through a T_1-contribution due to modulation of the crystalline contribution to the EFG from neighbour molecule reorientation, as we did successfully for 4-chloro-nitrobenzene [6], failed because in the 2-chloro-nitrobenzene we do not have orientational
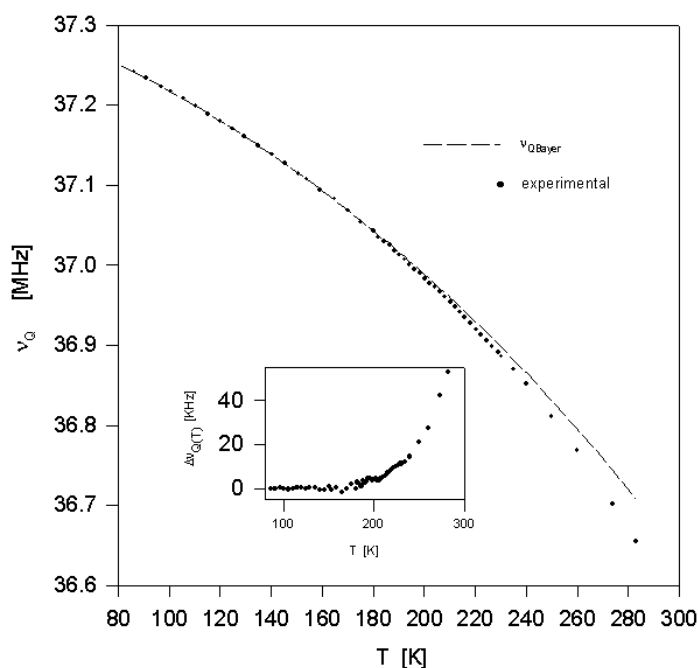
Figure 2. The temperature dependence of the NQR frequency of the ^{35}Cl in 2-chloro-nitrobenzene. The dashed curve represents the fit result using a torsional contribution (a Bayer–Kushida fit) in the 80–160 K interval. A noticeable departure from the vibrational model is observed in the high-temperature region. The window shows a nearly exponential departure of $\Delta \nu_Q(T) = \nu_Q^{Bayer} - \nu_Q^{med}$.

static disorder, as can be observed in the linewidth behaviour. The linewidth remains below the 7 kHz over the whole measurement range of temperatures. If we apply this formalism, we also obtain an unrealistic τ_r-value. This finding indicates that we must assume that a reorientation of the whole molecule cannot account for the spin–lattice relaxation in the high-temperature region.

3.2. NQR frequency

Experimental data on the temperature dependence of the NQR frequency of this compound, $\nu_Q(T)$, show no particular changes within a temperature region from 80 to 300 K (figure 2). A smooth, monotonically decreasing behaviour indicates that no first-order phase transition occurs in the measurement temperature range.

In the absence of phase transitions the NQR frequency is temperature dependent because the local EFG at the nuclear site is time averaged, from the molecular torsional oscillations [1]. The $\nu_Q(T)$ experimental data are usually well fitted by using a simple Bayer–Kushida [1] expression:

$$\nu_Q(T) = \nu_0 \left(1 - \frac{3}{2} \frac{\hbar^2}{kI\omega_t} \coth\left(\frac{\hbar\omega_t}{2kT}\right) \right) \tag{6}$$

where $\omega_t = \omega_0(1 - gT)$ is an average torsional frequency; ν_0 is the limiting static value of the resonance frequency and would represent the NQR frequency of a hypothetical rigid lattice; I is the average moment of inertia of the molecule, and the anharmonicity of the torsional oscillations has been taken into account as a temperature-dependent ω_t [7].

Any attempts to fit the $\nu_Q(T)$ data with only a Bayer–Kushida formula throughout the entire temperature range failed. Equation (6) can be fitted to our experimental data within a restricted temperature range $80 < T < 160$ K. The fitting parameters are compatible with

$$\nu_0 = 37.367 \text{ MHz} \qquad I = 9 \times 10^{-45} \text{ kg m}^2$$
$$\nu_t = 49 \text{ cm}^{-1} \qquad g = 1.12 \times 10^{-3} \text{ K}^{-1}.$$

These reasonable values show only a large and unexpected anharmonicity in the crystal. From 180 K we observed a deviation in the temperature dependence of $\nu_Q(T)$. This departure, although not too noticeable, is higher than our experimental error (more than 40 kHz at 280 K). The window in figure 2 shows the difference $\Delta\nu_Q(T)$ between experimental data and equation (6).

We observed in the high-temperature region a slope of $\nu_Q(T)$ larger than that found in the low-temperature region. This indicates that there is an extra contribution to the temperature dependence of ν_Q. The observed difference in the slope has a nearly exponential character that resembles that of a thermally activated mechanism, which follows an Arrhenius law. We ascribe this excess in the temperature coefficient to the EFG modulation due to hindered rotations of the NO_2 group.

3.3. Linewidth

The ^{35}Cl signal in the title compound yields a sharp, narrow, Lorentzian-shaped line. The linewidth of about 7 kHz at 80 K shows a slow narrowing when the temperature rises, probably due to a motional narrowing of the line arising from the torsional molecular oscillations. At temperatures close to 180–190 K the linewidth becomes more or less constant at about 4.5 kHz up to 230–240 K where a new slow line narrowing begins. This suggests that in the high-temperatures region there is an additional contribution to the linewidth that competes with the slow narrowing of the low-temperature region. It is probably due to a noticeable effect on $\Delta\nu_Q(T)$ from the decay of T_1 arising from the onset of NO_2 semirotation near the 200 K region.

4. Discussion

The aim of this work was to study, through the ^{35}Cl NQR, the movements of the NO_2 groups in a nitrobenzene molecule. In order to do so we chose the simplest system—that is, a nitrobenzene molecule where the closest hydrogen has been substituted for with chlorine. In this case in the V_{ij} at the chlorine site the steric effects of the NO_2 group will be present.

It is well known that the Hamiltonian of a quadrupole nucleus in an inhomogeneous electric field is

$$H_Q = \tfrac{1}{6} \sum_{i,j} Q_{ij} V_{ij}$$

where Q_{ij} are the elements of a tensor operator of the nuclear quadrupole moment and $V_{ij} = \partial^2 V / \partial x_i \, \partial x_j$ are the elements of the electric field gradient.

Following Seliger [3], we can split the time-dependent part of this Hamiltonian into two or more time-dependent contributions, where each complies with the respective perturbations to the V_{ij}. In this approach it is assumed that the time dependence of the spin Hamiltonian can be represented by a function of time:

$$H(t) = f(t)H^1 \tag{7}$$

where $f(t)$ is a random function that exchanges between two ($+1$ and -1) values. It is assumed also that

$$\langle V_{\pm i}(t) V_{\pm i}^*(t+\tau)\rangle = \langle V_{\pm i}(0) V_{\pm i}^*(0)\rangle \exp(-\tau/\tau_c) \tag{8}$$

and $\langle f(t)\rangle = 0$. In this case, Seliger's formalism gives a contribution to the spin–lattice relaxation:

$$T_1^{-1}|_{mod} = 4(BB^* + CC^*)\frac{\tau_c}{1+\omega_Q^2\tau_c^2} \tag{9}$$

where B and C are the off-diagonal elements of the perturbation Hamiltonian H^1. In $\tau_c = \tau_0 \exp(U/RT)$, the activation energy U and the lifetime τ_0 of an Arrhenius-like thermoactivated process are expressed by this perturbation Hamiltonian. In the case of a neighbouring molecular group reorientation, it is completely equivalent to that obtained by Woessner and Gutowsky (equation (2)) and q'/q is related to the Seliger $BB^* + CC^*$ element.

As regards the NQR frequency, Seliger also found that at very long correlation times ν_Q is shifted from its original value by a quantity

$$\Delta\nu_Q = \frac{BB^* + CC^*}{\pi\omega_Q}\frac{\omega_Q^2\tau_c^2}{1+\omega_Q^2\tau_c^2}. \tag{10}$$

Nitro group semirotation is only a special case of the application of the Seliger model. In fact, any movement of an electric charge distribution that can be accounted for by a Hamiltonian with an $f(t)$ function, as above, will yield a spin–lattice nuclear relaxation with a similar expression to equations (2) or (9).

Among the librational and nitro group semirotation relaxation processes, we observed in the ortho-chloro-nitrobenzene crystal an extra contribution to nuclear relaxation in the high-temperature region that cannot be explained by means of a whole-molecule reorientation. Consequently, we must think of the movement of a charge distribution near the chlorine site that modulates the EFG inducing a nuclear relaxation process. Abdel-Halim et al [8] found in another nitrobenzene, through second-harmonic-generation (SHG) study, some discrepancies between experimental results and thermal parameters resulting from refinement; such discrepancies can be explained if an orientational disorder of the NO_2 group is assumed— such as tipping or tilting of the nitro plane away from the plane of the aromatic ring, for steric reasons. In addition, Sharma et al [9] thought that the various phases found in the 1-chloro-2, 4-dinitrobenzene are no more than geometric isomers, due to different orientations of the NO_2 groups with respect to the ring system. The influence of such an orientational isomerism would also account for the various phases observed in this crystal.

We assume that in the 2-chloro-nitrobenzene this nitro group orientational disorder is dynamic, occurring by tilting or tipping of the nitro plane between two or more orientations. In this case we cannot anticipate a linewidth broadening and this meets the necessary requirements for applying Seliger's formalism. This orientational disorder would be independent of a possible $180°$ semirotation of the same atomic group, and we may assume that the onset of that dynamic orientational disorder will introduce an additional $T_1(T)$ contribution such as

$$T_1^{-1}|_x = \frac{1}{3}\left(\frac{q'}{q}\right)^2 \frac{\omega_Q^2\tau_x}{1+\omega_Q^2\tau_x^2} \tag{11}$$

where $\tau_x = \tau_x^0 \exp(U_x/RT)$ represents the Arrhenius-type thermoactivated process, with an activation energy U_x and a correlation time given by τ_x^0, of the disordering mechanism.

Figure 1 shows the result of a fit of the $T_1(T)$ data with an expression

$$T_1^{-1} = T_1^{-1}|_{lib} + T_1^{-1}|_{mod\,1} + T_1^{-1}|_{mod\,2} \tag{12}$$

where $T_1^{-1}|_{mod\,1}$ and $T_1^{-1}|_{mod\,2}$ are similar to the relaxation contributions arising from EFG modulation due to neighbouring NO_2 groups given by equations (2) or (11); each contribution to the nuclear relaxation is also depicted in the figure. The best-fit parameters obtained are

libration:	$a = 8 \times 10^{-5}$ s K^{-1}	$\lambda = 2.35$	
NO_2, mod 1:	$U = 21.9$ kJ mol^{-1}	$\tau_0 = 2.1 \times 10^{-14}$ s	$q'/q = 1.2 \times 10^{-3}$
NO_2, mod 2:	$U = 23.6$ kJ mol^{-1}	$\tau_0 = 4.1 \times 10^{-13}$ s	$q'/q = 2.9 \times 10^{-3}$.

The adjusted activation energies for these two proposed mechanisms turn out to be very similar; this makes us think that there is a coupling among these two movements of the nitro group. We consider them separately because the two mechanisms make major contributions but in different temperature ranges. This would indicate that they are independent, and therefore their contributions to the nuclear relaxation can be added.

The contributions to the temperature dependence of the ν_Q can be accounted for with an expression such as

$$\nu_Q(T) = \nu_Q(T)|_{Bayer} - \Delta\nu_Q(T)|_{mod\,1} - \Delta\nu_Q(T)|_{mod\,2} \tag{13}$$

where $\Delta\nu_Q(T)|_{mod\,1}$ and $\Delta\nu_Q(T)|_{mod\,2}$ stand for the effects on ν_Q arising from the nitro group movements with expressions given by equation (10). For the thermoactivated contributions to the temperature dependence, the best-fit parameters obtained by fitting equation (13) to frequency data lead to similar values to those from the $T_1(T)$ data fit. The Bayer contribution indicates a molecular oscillation in a highly anharmonic field (a g-value of 10^{-3} K^{-1}) with a torsional frequency around 57 cm^{-1}. The inertial moment would be $I \cong 6 \times 10^{-45}$ kg m^2 in agreement with that calculated from the molecular geometry for an oscillation around the axis normal to the Cl–C_2–C_5 direction.

5. Conclusions

We can apply the Seliger formalism to an orientational dynamic disorder of the NO_2 molecular group in the 2-chloro-nitrobenzene crystal. The unexplained high-temperature contributions to both $T_1(T)$ and $\nu_Q(T)$ for this compound can be accounted for by assuming a dynamic spatial disorder of the nitro plane away from the plane of the aromatic ring due to a competition between crystalline and steric chlorine effects. As far as we are aware, this experiment is the first direct observation of a dynamic disorder of nitrobenzene crystals due to the previously suggested tilting or tipping of the nitro group away from the benzene ring plane. Although we can observe noticeable effects on both nuclear relaxation time and resonance frequency arising from nitro group semirotation and also from tipping or tilting of the nitro plane, we cannot distinguish between them. In such a simple crystal as 2-chloro-nitrobenzene, the steric effect of the chlorine atom on the movements of the nitro group can be similar and thus make isolation and classification impossible. We should think of another experiment or system where, probably by crystalline symmetry considerations, we might distinguish the movements of tilting or tipping of the nitro plane away from the aromatic ring due to the semirotation around a N–C axis. X-ray crystal data on other nitrobenzenes suggest a kind of disorder, but the results are not conclusive [9]. Molecular crystals of dinitrochlorobenzenes or dichloronitrobenzenes where nitro groups occupy different positions with respect to the chlorine atoms in the ring, thus making the steric effects of chlorine on each NO_2 group stand out, are candidates likely to be amenable to such study.

Acknowledgments

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