where c_3 and c_4 are arbitrary constants of integration.

Now the solution turns out to be

$$\beta = aj_0(hR)\cos(ht+e_1)+bN_0(hR)\sin(ht+e_2) + \lambda R^2/4 + c_3\log R + c_4. \quad (18)$$

For Marder's metric,

$$ds^2 = e^{2\alpha-2\beta}(dT^2-dR^2) - R^2e^{-2\beta}d\phi^2 - (e^{2\beta}-e^{2\gamma})dZ^2, \quad (19)$$

the vacuum field equations yield

$$\alpha = 0$$
$$\beta'' + \beta'/R - \beta\cdot\cdot = \lambda$$
$$\gamma'' + \gamma'/R - \gamma\cdot\cdot = \lambda.$$

The form of γ is the same as that of β and hence we take $\gamma = n\beta$, n = constant etc. The solutions of (19) will be as in (16) and (18).

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^{13}C NMR AND NEW KINETIC EVIDENCE FOR STERIC ENHANCEMENT OF RESONANCE

V. BALIAH*, B. THEYMOLI and
A. MANGALAMUDAIYAR
Department of Chemistry, Annamalai University, Annamalainagar 608 002, India.
**Present address: 79 3rd Cross, Venkatanagar, Pondicherry 605 011, India.*

AFTER the discovery[1] that there is steric enhancement of resonance in *ortho*-substituted 4-nitroanisoles and similar compounds, more evidence was found[2-11] for the phenomenon. In this communication we present further evidence for it.

The second-order rate constants for the reaction between some substituted anilines and 2,4-dinitrochlorobenzene are given in table 1. This is a reaction in which extra electron displacements accompany

*For correspondence.

Table 1 *Second-order rate constants for the reaction between substituted anilines and 2,4-dinitrochlorobenzene at 30°C*

	$10^4\,k_2$ (l mol^{-1} s^{-1})	
Substituent(s)	Obs.	Calc.
H	1.10	–
4-Methoxy	11.4	–
3-Methyl	1.46	–
4-Methoxy-3-methyl	17.1	15.1
4-Methoxy-3,5-dimethyl	5.75	20.1

activation in consequence of electrical demands of the reaction centre. Thus electron-releasing groups, present *para* or *meta* to the amino group, increase the rate. The 4-methoxy group increases the rate by about ten times and the 3-methyl group by 1.3 times. When a methyl group is present *ortho* to methoxyl, the observed rate is 17.1×10^{-4}, l mol^{-1} s^{-1}, while the rate calculated on the basis of additivity of group effects[12] shows an increase of about 13%. The increased rate is due to the enhanced resonance of the methoxy group. When the methoxyl orients away from the *ortho* methyl, its rotation gets restricted and its chances of becoming coplanar with the benzene ring increase, enhancing its resonance.

The observed rate of 4-methoxy-3,5-dimethylaniline is much less than the calculated rate, indicating the expected steric inhibition of resonance.

Proof for the existence of steric enhancement of resonance may also be seen from the ^{13}C NMR spectra of the substituted 4-nitroanisoles listed in table 2. A 2-methyl substitution in 4-nitroanisole increases the electron density at C-4, compared with 4-nitroanisole, as seen from the upfield shift and $\Delta\delta$ value, reflecting steric enhancement of resonance. For 2,6-dimethyl-4-nitroanisole there is a downfield shift, indicating decreased electron density and the expected steric inhibition of resonance.

The compounds available commercially were purified rigorously before use and others were

Table 2 *Chemical shifts of the benzene ring for substituted anisoles*

	Chemical shift of C-4 (ppm)		
Anisole	Obs.	Calc.*	$\Delta\delta$
4-Nitro	141.5	140 8	+0 7
2-Methyl-4-nitro	140.6	140.7	−0 1
2,6-Dimethyl-4-nitro	143.2	140 6	+2.6

*Calculation is based on δ_e for benzene, 128 5, and substituent effects from ref. 15.

prepared by standard methods described in the literature. The purity was checked by TLC. The experimental procedure followed for the kinetic study was essentially that of Singh and Peacock[13], and Reinlander[14]. The spectra were recorded on a Bruker WM-300 instrument at 75 MHz in $CDCl_3$ and referenced to TMS.

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ISONITROSOTHIOCAMPHOR AS A SPECTROPHOTOMETRIC REAGENT FOR PLATINUM

P. K. PARIA, T. K. THOKDAR and S. K. MAJUMDAR
Department of Chemistry, North Bengal University, Darjeeling 734 430, India.

THE use of isonitrosothiocamphor (INTC) as an analytical reagent for palladium[1], cobalt[2] and copper[3] has been described earlier. At room temperature platinum (IV) shows no visible colour reaction with INTC, but forms a greenish chelate while heating on a water bath. The chelate is extractable into chloroform. A method has therefore been devised to determine platinum (IV) spectrophotometrically.

Isonitrosothiocamphor (INTC) was prepared by the reported method[4] and a solution of the reagent in ethanol (0.4%, w/v) was used. One gram of chloroplatinic acid (Johnson and Matthey) was dissolved in distilled water (100 ml) and was standardized[5]. Sample solutions of platinum were prepared by dilution of the stock solution.

Chloroform (E. Merck) was distilled before use. All other reagents used were of analytical grade. Stock solutions of the desired ions were prepared from the corresponding salts and the metal contents determined by conventional methods[5]. Potassium hydrogen phthalate sodium hydroxide buffer (pH 7–8) was used to adjust the pH of aqueous solutions. Absorbance and pH measurements were made as reported earlier[1].

To an aliquot of the sample solution of platinum (IV) (100–200 μg) was added ethanolic solution of INTC (0.5 ml of 0.4%), followed by addition of the buffer solution. The volume of the aqueous phase was maintained at 10 ml throughout the work. The mixture thus prepared was then heated (10 min) on a boiling water bath, cooled to room temperature, and then equilibrated (1 min) with chloroform (10 ml). The separated organic layer was poured over anhydrous sodium sulphate to remove any residual water. Finally the absorbance of the chloroform extract at 369 nm was measured against reagent blank. Platinum (IV) was determined from the calibration curve. To test for interference due to other ions, the ion was added to the system before addition of the reagent.

The extraction of platinum complex was investigated in the pH range 0-10. However, the chloroform extracts showed maximum and steady