

## INFRARED SPECTRA OF 2,4-DINITRO AND 2,6-DINITROANILINE DERIVATIVES

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Infrared absorption spectra of N-substituted derivatives of 2,4-dinitro- and 2,6-dinitroanilines have been measured and interpreted from the point of view of bond and sterical interactions of the substituted amino group with the both nitro groups.

Infrared spectra of 2,4-dinitro- and 2,6-dinitroanilines in the region of valence vibrations of nitro group are dealt with in two reports<sup>1,2</sup>. Frank, Hormann and Scheibe<sup>2</sup> used spectra of 2,4-dinitro- and 2,6-dinitroanilines and their N-methyl and N,N-dimethyl derivatives and a number of other polynitro compounds for detection of the absorption bands due to symmetrical and antisymmetrical valence vibrations of both *ortho* and *para* nitro group and discussed sterical and binding interactions. They stated that sterical effect of the substituted amino group in the dinitroanilines makes itself felt by a perturbation of conjugation between the *ortho* nitro group and the rest of the molecule. Several communications<sup>2-4</sup> deal with hydrogen bond between amino and nitro groups, however, they are mostly based on N—H bond frequencies of amino group. There are various views as to the existence of hydrogen bond; Dyall<sup>5</sup> contests its existence, whereas in a number of papers<sup>2,4,6,7</sup> the existence of hydrogen bond is admitted. A series of N-alkyl derivatives of 2,4-dinitroaniline and 2,4-dinitroaniline itself were measured in a region outside that of valence vibrations of nitro group<sup>3,4,8</sup>.

The present paper summarizes the studies of infrared spectra of N-substituted 2,4-dinitro- and 2,6-dinitroanilines which are discussed from the point of view of bond interactions of the amino and the both nitro groups and their sterical arrangement.

### EXPERIMENTAL

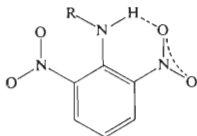
Purity of the compounds prepared by known procedures was checked by melting points and TLC (silica gel). The samples for IR measurements were prepared by the KBr technique (2 mg/1 g KBr). The spectra were measured with a Perkin-Elmer 621 recording spectrometer.

### RESULTS AND DISCUSSION

*Antisymmetrical valence vibrations of nitro group in 2,4-dinitro- and 2,6-dinitroanilines.* Absorption of valence antisymmetrical vibration of 2,4-dinitroanilines

is manifested in spectrum as a double absorption band of high intensity lying within the interval  $1\,542-1\,516\text{ cm}^{-1}$ . On the basis of the reports<sup>2,9</sup> the bands with wave numbers  $1\,542-1\,516$  and  $1\,517-1\,489\text{ cm}^{-1}$  were assigned to *ortho* and *para* nitro groups, respectively. With the non-substituted and the N-monosubstituted 2,4-dinitroanilines the absorption band of antisymmetrical vibration of *ortho* nitro group lies in a relatively narrow interval of  $10\text{ cm}^{-1}$  (with aliphatic substituents  $6\text{ cm}^{-1}$  only). No correlation was found between bulkiness of substituent or number of its carbon atoms and position of the absorption band. The N-aryl substituted compounds absorb at somewhat lower frequencies due probably to the extended conjugated system (another aromatic nucleus)<sup>10-12</sup>. Steric effect was not observed with N-isopropyl- and N-isobutyl-2,4-dinitroanilines, but in corresponding N,N-disubstituted 2,4-dinitroanilines it makes itself felt by a small shift of the absorption band of antisymmetrical valence vibration of *ortho* and *para* nitro group towards higher frequency values. In contrast therewith some authors<sup>13,24</sup> studying sterical distortions of nitro group arrived at the conclusion that only the valence symmetrical vibration is affected more markedly, whereas the antisymmetrical vibration is either unchanged or slightly lowered by sterical distortion of nitro group<sup>15</sup>. Thus the increase in frequency of valence antisymmetrical vibration of *ortho* nitro group in the dinitroanilines must be explained by lowering of N—O bond order and simultaneous increasing of O—N—O bond angle due to mutual sterical interactions of nitro and amino groups. Perhaps it is also significant that hydrogen bond between *ortho* nitro group and amino group is weakened by electron-acceptor effect of the *para*-standing nitro group.

Valence antisymmetrical vibration of *para* nitro group of 2,4-dinitroanilines makes itself felt by an intensive absorption band within  $1\,517$  to  $1\,489\text{ cm}^{-1}$ . With the non-substituted 2,4-dinitroaniline its intensity is the same as that of *ortho* nitro group, with the N-monosubstituted compounds it is lower, and with the N,N-disubstituted ones it is higher. Upper part of the absorption band shows a fine structure indicating a superposition of absorptions of two or more different structures of the molecule. Position of the absorption band (except for the N,N-dimethyl derivative) is not sensitive to effects of sterically active substituents. The compounds with aromatic substituents show a slight frequency lowering due to increased conjugation of the both nuclei.



SCHEME 1

The absorption due to antisymmetrical valence vibration of *ortho* nitro groups of 2,6-dinitroanilines is manifested by intensive bands in the region 1 517 to 1 496  $\text{cm}^{-1}$ . Shape of the absorption bands is changed according to number of substituents at nitrogen. The parent and the N-monosubstituted 2,6-dinitroaniline show two overlapping bands, the N,N-disubstituted compounds show one broad band with fine structure. The two absorption bands of N-monosubstituted 2,6-dinitroanilines are due to structure of nitro groups. It is presumed that one nitro group lies in the plane of the benzene nucleus due to weak hydrogen bond (Scheme 1). The other nitro group is deviated out of this plane by sterical distortion of the substituent, which is manifested by an independent spectral band of higher wave number.

In the case of the N,N-disubstituted 2,6-dinitroanilines it also cannot be presumed that the both nitro groups are equivalent in their sterical arrangement. Broad absorption bands containing absorptions of two frequencies (or more frequencies in the case of diethylamino and piperidino derivatives) indicate that mutual sterical

TABLE I

Wave numbers of valence vibrations of nitro groups of N-substituted 2,4- and 2,6-dinitroanilines ( $\text{cm}^{-1}$ )

Compound	Substituted aniline	$\nu_{\text{as}}(\text{o-NO}_2)$	$\nu_{\text{as}}(\text{p-NO}_2)$	$\nu_{\text{s}}(\text{o-NO}_2)$	$\nu_{\text{s}}(\text{p-NO}_2)$
I	2,4-dinitro-	1 527	1 501	1 336	1 303
II	N-methyl-2,4-dinitro-	1 525	1 496	1 331	1 310
III	N-ethyl-2,4-dinitro-	1 528	1 505	1 337	1 307
IV	N-butyl-2,4-dinitro-	1 522	1 500	1 333	1 313
V	N-isopropyl-2,4-dinitro-	1 527	1 510	1 331	1 310
VI	N-isobutyl-2,4-dinitro-	1 527	1 506	1 337	1 311
VII	N,N-dimethyl-2,4-dinitro-	1 542	1 517	1 338	1 323
VIII	N,N-diethyl-2,4-dinitro-	1 532	1 506	1 337	1 320
IX	N-methyl-N-phenyl-2,4-dinitro-	1 533	1 496	1 323	1 286
X	N-2-aminophenyl-2,4-dinitro-	1 519	1 502	1 441	1 308
XI	N-phenyl-2,4-dinitro-	1 521	1 500	1 338	1 310
XII	N-1-naphthyl-2,4-dinitro-	1 518	1 489	1 335	1 304
XIII	N,N-diphenyl-2,4-dinitro-	1 516	1 490	1 339	1 308
XIV	2,6-dinitro-	1 517	—	1 360	—
XV	N-methyl-2,6-dinitro-	1 504	—	1 340	—
XVI	N-ethyl-2,6-dinitro-	1 496	—	1 343	—
XVII	N,N-dimethyl-2,6-dinitro-	1 520	—	1 350	—
XVIII	N,N-diethyl-2,6-dinitro-	1 517	—	1 348	—
XIX	N-cyclohexyl-2,6-dinitro-	1 498	—	1 341	—
XX	N-phenyl-2,6-dinitro-	1 502	—	1 347	—

interactions of amino and nitro groups result in torsional buckling around their C—N bonds and, in the case of the substituted amino group, also deflection from the symmetry axis of the molecule. Simultaneously its nitrogen atom changes from  $sp^2$  to  $sp^3$  hybridization, and its internal rotation enables to form (with nitro group) conformational isomers, which results in broadening and/or splitting of the absorption bands. However, sterical distortion of substituents cannot account for the presence of two intensive absorption bands lying in the region of frequencies of anti-symmetrical valence vibrations of non-substituted 2,6-dinitroaniline. Its molecule can be considered planar in analogy to *o*-nitroaniline in which the planar structure was confirmed on the basis of polarization infrared spectra. This structure is convenient from the point of view of symmetry and is supported by formation of weak hydrogen bridges. The non-equivalence of the two nitro groups could be derived *e.g.* from different strength of hydrogen bonds, but there is no experimental evidence for it, and the N—H valence vibrations do not indicate it either<sup>3,16</sup>.

*Symmetrical valence vibrations of nitro group of 2,4-dinitro- and 2,6-dinitroanilines.* In the frequency region of symmetrical valence vibrations there are several very intensive absorption bands in spectra of 2,4-dinitroanilines. Due to electron-donor action of amino group the lower frequency belongs to *para* nitro group and the higher one belongs to *ortho* nitro group. The absorption intensity is greatest out of the whole spectrum<sup>9</sup>.

Frequency of *ortho* nitro group lies within a very narrow interval (1 339 to 1 331  $\text{cm}^{-1}$ ) except for N-methyl-N-phenyl derivative IX (1 323  $\text{cm}^{-1}$ ). The unexpectedly narrow frequency interval for both mono- and disubstituted 2,4-dinitroanilines is surprising, because just with this vibration the sterical effect of substituents at the amino group should be most marked<sup>14,15</sup>.

The nitro group at *para* position absorbs within a somewhat broader interval (1 323–1 303  $\text{cm}^{-1}$ ). The lowest frequency is that of the parent compound I and the highest one belongs to the N,N-disubstituted compound VII. The compound IX forms an exception, having both its symmetrical and antisymmetrical valence vibration shifted towards lower values of wave number due to conjugation.

Symmetrical valence vibration of nitro group should reflect the sterical effect of the adjacent substituent by exhibiting a far greater shift to higher energies than the antisymmetrical valence vibration does<sup>14,17</sup>. Its unusual behaviour, *i.e.* slight response to effect of bulkier substituents at amino group, is due to specific property of this vibration. In contrast to antisymmetrical valence vibration whose frequency is determined by the N—O bond order (and in this way it expresses changes in inductive and resonance effects) the force constant of symmetrical valence vibration of nitro group involves also a contribution<sup>29</sup> of the force constant of  $C_{Ar}$ —NO<sub>2</sub> bond. Hence the frequency is influenced by order of the both bonds, the responses of the two bonds to sterical hindrance of mesomeric interaction between nitro group

TABLE II  
Infrared spectra of N-substituted 2,4- and 2,6-dinitroanilines

Compound	Substituted aniline	Wave numbers
I	2,4-dinitro-	3 435 vs, 3 322 vs, 1 635 vs, 1 591 vs, 1 575 m, 1 474 m, 1 431 s, 1 390 s, 1 262 vsb, 1 063 s, 1 018 m, 926 m, 919 m, 811 w, 712 m, 694 w, 639 m, 584 s, 437 w, 422 w, 405 w
II	N-methyl-2,4-dinitro-	3 328 m, 1 625 vs, 1 577 m, 1 535 m, 1 472 m, 1 465 w, 1 451 m, 1 432 w, 1 410 s, 1 385 w, 1 365 m, 1 274 sb, 1 228 sb, 1 172 s, 1 068 s, 1 041 s, 923 m, 912 m, 792 w, 700 m, 645 m, 531 w, 432 w
III	N-ethyl-2,4-dinitro-	3 351 s, 1 622 vs, 1 550 w, 1 477 s, 1 454 w, 1 428 s, 1 424 s, 1 398 w, 1 379 w, 1 354 m, 1 236 sb, 1 172 s, 1 161 s, 1 090 s, 1 061 m, 1 049 m, 981 w, 931 w, 919 w, 908 w, 819 w, 776 w, 709 w, 696 w, 665 w, 654 w, 639 w, 594 w, 541 w, 485 w
IV	N-butyl-2,4-dinitro-	3 339 m, 1 626 vs, 1 542 w, 1 477 w, 1 466 w, 1 460 w, 1 454 w, 1 431 m, 1 420 s, 1 383 w, 1 367 m, 1 338 s, 1 297 sb, 1 269 sb, 1 240 mb, 1 225 mb, 1 168 m, 1 151 m, 1 070 m, 1 048 m, 922 m, 821 w, 797 m, 781 m, 711 w, 700 w, 664 w, 650 w, 642 w, 588 w, 514 w, 492 w, 477 w
V	N-isopropyl-2,4-dinitro-	3 310 m, 1 625 vs, 1 518 s, 1 469 w, 1 420 m, 1 389 m, 1 376 m, 1 365 m, 1 249 sb, 1 225 mb, 1 161 s, 1 058 s, 958 w, 917 s, 826 m, 714 m, 688 w, 649 s, 637 s, 529 w, 486 w, 458 w, 438 w
VI	N-isobutyl-2,4-dinitro-	3 345 s, 1 626 vs, 1 548 w, 1 494 m, 1 483 w, 1 472 w, 1 447 w, 1 421 s, 1 393 w, 1 385 w, 1 370 s, 1 301 sb, 1 250 vs, 1 236 vs, 1 171 m, 1 079 m, 1 045 w, 951 w, 923 m, 906 w, 826 m, 789 w, 700 m, 676 m, 639 m, 544 w, 508 w, 426 w
VII	N,N-dimethyl-2,4-dinitro-	1 613 vs, 1 511 vs, 1 503 s, 1 475 s, 1 460 w, 1 450 w, 1 435 m, 1 421 m, 1 385 m, 1 367 s, 1 351 m, 1 347 m, 1 303 vs, 1 229 m, 1 177 w, 1 151 s, 1 060 s, 958 m, 951 m, 911 w, 806 m, 798 m, 716 w, 658 w, 629 w, 588 w, 541 w, 487 w, 407 w, 426 w
VIII	N,N-diethyl-2,4-dinitro-	1 607 vs, 1 485 m, 1 460 m, 1 454 w, 1 427 w, 1 401 w, 1 384 m, 1 355 s, 1 260 m, 1 189 m, 1 144 s, 1 063 s, 1 012 w, 965 w, 939 w, 905 w, 819 w, 787 w, 721 w, 658 w, 639 w, 588 w, 541 w, 494 w, 467 w, 427 w, 403 w

TABLE II  
(Continued)

Compound	Substituted aniline	Wave numbers
<i>IX</i>	N-methyl-N-phenyl- -2,4-dinitro-	1 609 vs, 1 457 w, 1 454 w, 1 446 w, 1 433 w, 1 421 w, 1 384 w, 1 362 s, 1 355 s, 1 266 m, 1 240 m, 1 177 w, 1 082 s, 1 069 m, 1 042 m, 1 024 w, 1 001 w, 975 w, 927 m, 906 w, 866 w, 845 w, 769 m, 720 w, 704 w, 696 m, 664 w, 642 w, 618 w, 558 w, 479 w, 458 w, 440 w
<i>X</i>	N-2-aminophenyl- -2,4-dinitro-	3 429 s, 3 341 s, 1 622 vs, 1 460 m, 1 420 vs, 1 385 w, 1 358 s, 1 227 s, 1 213 m, 1 145 vs, 1 060 s, 1 031 w, 976 w, 930 m, 881 w, 860 w, 699 m, 659 m, 634 m, 585 m, 514 s, 479 m, 469 m
<i>XI</i>	N-phenyl-2,4-dinitro-	3 300 s, 1 624 s, 1 551 w, 1 496 s, 1 461 w, 1 426 s, 1 388 w, 1 326 vs, 1 271 sb, 1 227 mb, 1 218 m, 1 178 w, 1 058 m, 1 027 m, 1 003 w, 995 w, 960 w, 923 m, 908 w, 843 w, 824 w, 818 w, 716 w, 690 m, 683 m, 669 w, 628 m, 559 w, 526 w, 498 w, 425 w, 407 w
<i>XII</i>	N-1-naphthyl-2,4-dinitro-	3 302 m, 1 619 vs, 1 543 w, 1 510 s, 1 464 w, 1 446 w, 1 422 s, 1 391 w, 1 381 w, 1 331 vs, 1 271 mb, 1 258 m, 1 243 m, 1 221 w, 1 199 w, 1 170 w, 1 082 w, 1 058 m, 1 046 w, 1 020 w, 989 w, 965 w, 913 m, 822 w, 788 m, 772 s, 712 w, 666 w, 637 w, 615 w, 576 w, 559 w, 528 w, 501 w, 460 w, 427 w
<i>XIII</i>	N,N-diphenyl-2,4-dinitro-	1 617 s, 1 538 s, 1 486 vs, 1 480 s, 1 452 m, 1 420 w, 1 385 w, 1 339 vs, 1 242 m, 1 186 w, 1 177 w, 1 170 w, 1 071 m, 1 027 w, 980 w, 971 w, 941 w, 919 w, 900 m, 897 w, 712 w, 694 s, 665 w, 647 w, 638 w, 621 w, 589 m, 537 m, 500 w, 469 w, 426 w, 407 w
<i>XIV</i>	2,6-dinitro-	3 439 m, 3 329 m, 1 643 s, 1 567 s, 1 528 vs, 1 518 vs, 1 450 m, 1 437 m, 1 386 w, 1 360 m, 1 335 w, 1 302 m, 1 268 vsb, 1 164 w, 1 109 w, 1 036 w, 977 w, 890 s, 860 w, 796 w, 733 s, 604 w, 542 m, 524 w, 479 w.
<i>XV</i>	N-methyl-2,6-dinitro-	3 368 s, 3 362 s, 1 625 s, 1 457 s, 1 445 m, 1 419 m, 1 405 m, 1 383 m, 1 272 vsb, 1 048 m, 975 w, 913 m, 843 w, 804 w, 798 w, 736 m, 728 s, 634 m, 580 m, 549 w, 489 w, 466 w
<i>XVI</i>	N-ethyl-2,6-dinitro-	3 326 w, 3 312 w, 1 622 s, 1 540 m, 1 475 m, 1 442 s, 1 411 w, 1 382 w, 1 279 vsb, 1 250 sb, 1 200 m, 1 156 w, 1 055 m, 941 m, 913 s, 864 w, 859 w, 829 m, 792 m, 754 m, 740 vs, 714 vs, 647 m, 636 m, 590 m, 546 w, 525 w, 447 w

TABLE II  
 (Continued)

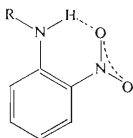
Compound	Substituted aniline	Wave numbers
XVII	N,N-dimethyl-2,6-dinitro-	1 612 s, 1 465 m, 1 456 m, 1 452 m, 1 440 m, 1 420 m, 1 385 w, 1 294 m, 1 280 m, 1 252 m, 1 212 w, 1 179 w, 1 168 w, 1 068 w, 960 s, 912 m, 833 m, 811 s, 747 s, 719 w, 703 m, 696 s, 591 m, 544 m
XVIII	N,N-diethyl-2,6-dinitro-	1 614 s, 1 563 m, 1 553 vs, 1 468 s, 1 456 m, 1 450 m, 1 382 m, 1 371 s, 1 299 m, 1 291 m, 1 279 s, 1 237 m, 1 174 m, 1 152 w, 1 098 m, 1 078 w, 1 061 w, 1 029 w, 952 w, 905 m, 838 m, 808 m, 784 w, 744 s, 737 m, 709 m, 698 m, 541 w
XIX	N-cyclohexyl-2,6-dinitro-	3 420 w, 3 290 w, 1 611 s, 1 547 m, 1 470 m, 1 448 s, 1 445 s, 1 417 w, 1 385 w, 1 368 w, 1 281 sb, 1 264 sb, 1 249 sb, 1 212 m, 1 174 w, 1 154 w, 1 140 w, 1 076 w, 1 052 w, 914 m, 859 m, 841 w, 899 m, 799 m, 736 s, 711 s, 639 w, 563 w, 544 w, 520 w, 484 w
XX	N-phenyl-2,6-dinitro-	3 301 s, 1 617 m, 1 580 m, 1 521 vs, 1 502 vs, 1 454 m, 1 444 m, 1 408 w, 1 385 w, 1 347 s, 1 313 w, 1 300 m, 1 281 mb, 1 267 mb, 1 223 m, 1 189 m, 1 166 m, 1 159 w, 1 123 m, 1 099 m, 1 072 m, 928 w, 902 w, 893 w, 811 w, 759 w, 730 m, 711 w, 702 w, 691 m, 607 w, 576 w, 541 w, 496 m, 409 w

and benzene nucleus being opposite: the  $C_{Ar}-NO_2$  bond order is decreased, whereas the N—O bond order is increased.

Another factor which can contribute to lowering of frequency of symmetrical valence vibration of nitro group and its response to sterical effect is derived from so called valence deflection hypothesis<sup>17</sup>. According to this theory a nitro group having a bulky substituent next to it (*e.g.* alkyl) is deflected from this substituent, and no frequency increase takes place<sup>14</sup>. In the case of *ortho* nitro-N, N-disubstituted derivatives of compound I it can be presumed that localization of neither nitro nor amino group takes place. Then the frequency of *ortho* nitro group remains unchanged even in the N,N-disubstituted derivatives, whereas with *para* nitro group it is somewhat increased due to delocalization of free electron pair.

The third factor which may play a certain role in steric hindrance of mesomeric interaction between the nitro groups and benzene nucleus is the pseudo-cyclic arrangement (Formula 2) based on hydrogen bond. Although this bond is weak

due to decreased acidity of N—H bond in dinitroanilines, its existence can have a certain influence on the N—O bond order and C<sub>Ar</sub>—NO<sub>2</sub> bond order.



SCHEME 2

Frequency of symmetrical valence vibration of nitro group of 2,6-dinitroanilines lies within the interval 1360–1340 cm<sup>-1</sup>. The N-monosubstituted compounds absorb at lower frequencies (the N-phenylderivative *XX* 1347 cm<sup>-1</sup>, N-alkyl-derivatives *XV*, *XVI* 1343–1340 cm<sup>-1</sup>), the N,N-disubstituted compounds *XVII*,

TABLE III

Wave numbers of C<sub>Ar</sub>—NO<sub>2</sub> and C<sub>Ar</sub>—NH<sub>2</sub> valence vibrations of N-substituted 2,4- and 2,6-dinitroanilines

Compound	Substituted aniline	Wave numbers		
		C <sub>Ar</sub> —NO <sub>2</sub> ( <i>para</i> )	C <sub>Ar</sub> —NO <sub>2</sub> ( <i>ortho</i> )	C <sub>Ar</sub> —NH <sub>2</sub>
<i>I</i>	2,4-dinitro-	1 133	1 126	1 289
<i>II</i>	N-methyl-2,4-dinitro-	1 137	1 111	1 287
<i>III</i>	N-ethyl-2,4-dinitro-	1 137	1 111	1 276
<i>IV</i>	N-butyl-2,4-dinitro-	1 138	1 114	1 281
<i>V</i>	N-isopropyl-2,4-dinitro-	1 141	1 113	1 284
<i>VI</i>	N-isobutyl-2,4-dinitro-	1 135	1 114	1 270
<i>VII</i>	N,N-dimethyl-2,4-dinitro-	1 118	1 096	1 271
<i>VIII</i>	N,N-diethyl-2,4-dinitro-	1 127	1 092	1 281
<i>IX</i>	N-methyl-N-phenyl-2,4-dinitro-	1 134	1 118	1 286
<i>X</i>	N-2-aminophenyl-2,4-dinitro-	1 132	1 117	1 276
<i>XI</i>	N-phenyl-2,4-dinitro-	1 145	1 126	1 284
<i>XII</i>	N-1-naphthyl-2,4-dinitro-	1 143	1 130	1 280
<i>XIII</i>	N,N-diphenyl-2,4-dinitro-	1 156	1 135	1 283
<i>XIV</i>	2,6-dinitro-	—	1 109	1 268
<i>XV</i>	N-methyl-2,6-dinitro-	—	1 111	1 278
<i>XVI</i>	N-ethyl-2,6-dinitro-	—	1 117	1 279
<i>XVII</i>	N,N-dimethyl-2,6-dinitro-	—	1 110	1 280
<i>XVIII</i>	N,N-diethyl-2,6-dinitro-	—	1 117	1 279
<i>XIX</i>	N-cyclohexyl-2,6-dinitro-	—	1 106	1 281
<i>XX</i>	N-phenyl-2,6-dinitro-	—	1 106	1 281



*XVIII* absorb at higher frequencies (1 350–1 348  $\text{cm}^{-1}$ ). As compared with the frequencies of *ortho* nitro group in N-substituted 2,4-dinitroanilines (1 337–1 331  $\text{cm}^{-1}$  for N-monosubstituted compounds *II*, *III* and 1 338–1 337  $\text{cm}^{-1}$  for N, N-disubstituted derivatives *VII*, *VIII*), symmetrical vibration of 2,6-dinitroanilines reflects the steric effect of the substituted amino group by a far more marked frequency increase.

Steric distortion of nitro group in the series of 2,6-dinitroanilines is obvious already with the N-monosubstituted derivatives. This is obviously due to alkylamino group being fixed in the plane of the molecule by hydrogen bridge with nitro group and having no possibility to deviate from the second nitro group. Thus the structure (Scheme 1) with non-equivalent nitro groups is formed according to which each nitro group should be assigned its own frequency. This is why the given frequency intervals belong to nitro group next to alkyl group. Symmetrical valence vibration of 6-nitro group cannot be unambiguously considered to be involved in absorption band of the other nitro group or in intensive and very broad absorption band within 1 300 to 1 225  $\text{cm}^{-1}$  which is due to the pseudo-cyclic structure (Scheme 1) formed by the mentioned intramolecular hydrogen bridge.

*Characteristical valence vibrations of 2,4-dinitro- and 2,6-dinitroanilines with non-substituted and mono-substituted amino group.* The compounds containing at least one hydrogen atom at the nitrogen of amino group exhibit a very broad intensive absorption band in the region 1 300 to 1 225  $\text{cm}^{-1}$  which is composed of several overlapping absorptions reaching (in some cases) up to the region of frequencies of symmetrical valence vibration of nitro group. Absorption bands of a similar character were observed also with 2-nitroaniline and 2-nitrophenol<sup>16</sup>. This frequency can be denoted as characteristic of the pseudo-cyclic arrangement (Scheme 2) formed by interaction of oxygen of nitro group with amino group *via* hydrogen bridge. From polarization spectra of oriented crystals of 2-nitrophenol and 2-nitroaniline<sup>16</sup> it follows that polarization characteristics of this absorption are identical with those of the bonds lying in the plane of the molecule. This fact agrees with the structure (Scheme 2) according to which nitro and amino groups are coplanar.

The parent 2,6-dinitroaniline exhibits an unusually high ratio of the area of the discussed absorption band to that of symmetrical valence vibration as compared with the N-monosubstituted derivatives. This fact indicates that also the second nitro group is partially connected with amino group through hydrogen bridge.

*Skeletal vibrations of C—C bonds.* These vibrations are presented by four vibration modes designed (according to vibration scheme of benzene nucleus<sup>28</sup>) with the numbers 8a, 8b, 19a, 19b. The frequencies of the vibrations 8a and 8b are found within the intervals 1 632 to 1 610  $\text{cm}^{-1}$  and 1 593 to 1 579  $\text{cm}^{-1}$  for 2,4-dinitroanilines and within the intervals 1 646 to 1 612  $\text{cm}^{-1}$  and 1 583 to 1 567  $\text{cm}^{-1}$  for 2,6-dinitroanilines.

The absorption corresponding to the 8a vibration is very weak in most cases. However, in the case of dinitroanilines it forms medium to very high intensive bands due to substitution of benzene nucleus by heavy nitro groups. Frequency of this vibration is markedly lower with the disubstituted compounds than with the monosubstituted ones, this decrease being more marked with 2,6-dinitroanilines. Hence this case exhibits a steric interaction between dialkylamino group and vicinal nitro group *via* a change in  $\pi$ -electron system of the molecule.

Intensity of skeletal vibration 8a of 2,4-dinitroanilines is comparable with that of antisymmetrical valence vibration of nitro group, hence it belongs to the most intensive spectral bands. With 2,6-dinitroanilines its intensity is medium and its frequency is shifted towards lower energies.

Out of the two remaining vibrations of aromatic ring denoted as 19a, 19b, the latter only is distinct. It is found within the intervals 1 432–1 420 and 1 450–1 442

TABLE IV

The other wave numbers of N-substituted 2,4- and 2,6-dinitroanilines

Com- pound	Substituted aniline	Type of vibration			
		wagging NO <sub>2</sub>	scissoring NO <sub>2</sub>	rocking NO <sub>2</sub>	skeletal 8a
<i>I</i>	2,4-dinitro-	762	740	523	1 591
<i>II</i>	N-methyl-2,4-dinitro-	761	741	517	1 589
<i>III</i>	N-ethyl-2,4-dinitro-	760	740	529	1 591
<i>IV</i>	N-butyl-2,4-dinitro-	758	740	523	1 588
<i>V</i>	N-isopropyl-2,4-dinitro-	756	738	520	1 593
<i>VI</i>	N-isobutyl-2,4-dinitro-	758	738	525	1 589
<i>VII</i>	N,N-dimethyl-2,4-dinitro-	752	739	516	1 583
<i>VIII</i>	N,N-diethyl-2,4-dinitro-	754	737	525	1 579
<i>IX</i>	N-methyl-N-phenyl-2,4-dinitro-	754	742	527	1 589
<i>X</i>	N-2-aminophenyl-2,4-dinitro-	759	746	526	1 589
<i>XI</i>	N-phenyl-2,4-dinitro-	758	745	517	1 588
<i>XII</i>	N-1-naphthyl-2,4-dinitro-	749	739	515	1 584
<i>XIII</i>	N,N-diphenyl-2,4-dinitro-	755	736	516	1 590
<i>XIV</i>	2,6-dinitro-	—	—	—	1 567
<i>XV</i>	N-methyl-2,6-dinitro-	—	—	—	1 573
<i>XVI</i>	N-ethyl-2,6-dinitro-	—	—	—	1 572
<i>XVII</i>	N,N-dimethyl-2,6-dinitro-	—	—	—	1 567
<i>XVIII</i>	N,N-diethyl-2,6-dinitro-	—	—	—	1 578
<i>XIX</i>	N-cyclohexyl-2,6-dinitro-	—	—	—	1 583
<i>XX</i>	N-phenyl-2,6-dinitro-	—	—	—	1 580

$\text{cm}^{-1}$  for 2,4- and 2,6-dinitroanilines, respectively. The 19a vibration should be found in the region about  $1\,420\text{ cm}^{-1}$ , however, with some derivatives it is not distinct due to its little intensity. Its detection is made difficult by the fact that vibration of other bonds is observed in this region (e.g. deformation vibration of C—H bond).

*The remaining vibrations of dinitroanilines.* Out of the vibrations having some relation to nitro group the most important is the  $\text{C}_{\text{Ar}}\text{—NO}_2$  bond vibration. Several authors<sup>7,18,19</sup> locate its absorption near  $850\text{ cm}^{-1}$ . In later communications there appears doubt about this assignment because of insensitivity to substitution of the aromatic nucleus<sup>18,20</sup>, and the frequency is assigned to scissoring vibration of nitro group<sup>21</sup>. Katritzki and Simmons<sup>9</sup> and van Veen and coworkers<sup>14</sup> analyzed a great number of nitro compounds without concluding the problem of frequency of  $\text{C}_{\text{Ar}}\text{—NO}_2$  bond vibration. Pinchas and coworkers<sup>21</sup> assign this vibration to the frequency  $1\,109\text{ cm}^{-1}$  on the basis of spectra of nitrobenzene containing <sup>15</sup>N and <sup>18</sup>O isotopes. Mooney<sup>22</sup> arrived at the same conclusion, being also able to assign definitively the frequency  $850\text{ cm}^{-1}$  to the scissoring vibration of nitro group.

The out-of-plane deformation vibration of nitro group of 2,4-dinitroanilines (wagging) was assigned the vibration region  $784\text{—}703\text{ cm}^{-1}$  ( $755\text{ cm}^{-1}$  for *p*-nitroaniline<sup>23–25</sup>), rocking vibration of nitro group was assigned the region  $535\text{—}532\text{ cm}^{-1}$  (refs<sup>21,26–29</sup>) or  $571\text{—}508\text{ cm}^{-1}$  (refs<sup>23,24</sup>).

On the contrary, Pinchas, Samuel and Silver<sup>21</sup> assigned the out-of-plane deformation vibration of nitro group in nitrobenzene to the frequency  $532\text{ cm}^{-1}$  and the rocking vibration of nitro group to the frequency  $417\text{ cm}^{-1}$ .

Table IV gives the frequencies assigned by us to the mentioned vibrations of nitro group in spectra of nitroanilines.

Valence vibration of the bond between amino group and benzene nucleus (similar to that of  $\text{C}_{\text{Ar}}\text{—NO}_2$  bond) denoted as “X-sensitive vibration of benzene ring” mixed with valence vibration of  $\text{C}_{\text{Ar}}\text{—NH}_2$  bond has the frequency value  $1\,279\text{ cm}^{-1}$  for aniline. For 2,4- and 2,6-dinitroanilines it is in the intervals  $1\,289\text{—}1\,270\text{ cm}^{-1}$  and  $1\,281\text{—}1\,268\text{ cm}^{-1}$ , respectively.

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