Refinement of the disordered structures

β-nitrostyrene (1)

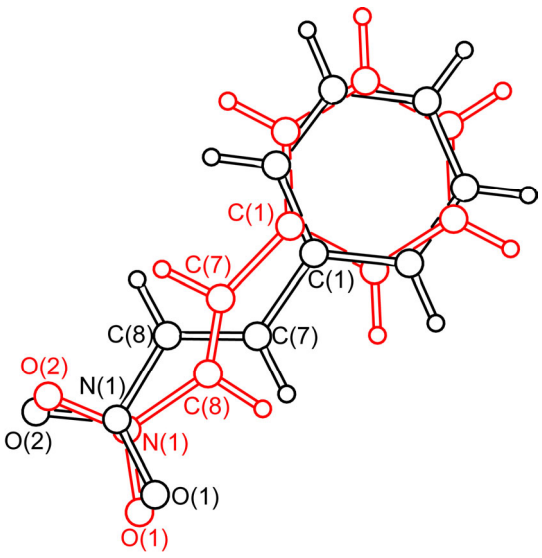
The disordered molecules of **1** were refined as follows. The benzene ring of the minor conformer was constrained to be a regular hexagon with bond lengths of 1.39 Å. H atoms were refined according to the riding model.

In order to avoid the distortion of the structures, especially that of the minor conformer, the following lengths were restrained using SHELXL DFIX instructions. The observed lengths of the corresponding bonds of 4-methoxy-β-nitrostyrene (**3**) at 90 K, the structure of which is free from disorder, were used as the target values of the restraints. The length of the C–Ph bond (C(1)–C(7)) of the two conformers was restrained to be 1.45 Å with an e.s.d. of 0.01 Å. The length of the C–NO_2 bond (C(8)–N(1)) of the two conformers was restrained to be 1.44 Å with an e.s.d. of 0.01 Å. The lengths of the N–O bonds (N(1)–O(1) and N(1)–O(2)) of the two conformers were restrained to be 1.23 Å with an e.s.d. of 0.01 Å.

For the same reason as above, the atomic distance C(7)…N(1) of the two conformers was restrained to be equal with an e.s.d. of 0.01 Å using SHELXL SADI instruction in order to restrain the bond angle C(7)–C(8)–N(1) of the two conformers to be equal.

Non-H atoms of the major conformer were refined anisotropically at all temperatures. At 300, 250, and 200 K, non-H atoms of the minor conformer were refined isotropically. At 150 and 90 K, non-H atoms of the minor conformer were refined isotropically using a common temperature factor for all the C and N atoms and another isotropic temperature factor for the O atoms.

Populations were determined from the same refinement as above, except that all atoms were refined isotropically using a common temperature factor for all the C and N atoms and another isotropic temperature factor for the O atoms. The populations were held constant during the subsequent anisotropic refinement.



4-dimethylamino-β-nitrostyrene (2)

The disordered molecules of **2** were refined as follows. The benzene ring of the minor conformer was constrained to be a regular hexagon with bond lengths of 1.39 Å. H atoms were refined according to the riding model.

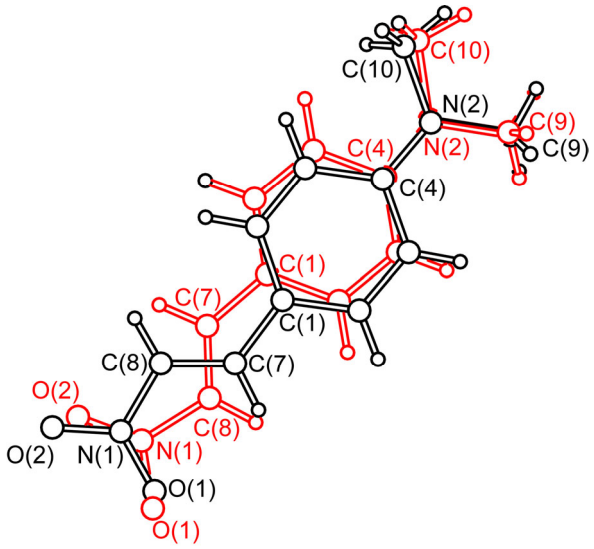
In order to avoid the distortion of the structures, especially that of the minor conformer, the following lengths were restrained using SHELXL DFIX instructions. The observed lengths of the corresponding bonds of 4-methoxy-β-nitrostyrene (**3**) at 90 K were used as the target values of the restraints. The length of the C–Ph bond (C(1)–C(7)) of the two conformers was restrained to be 1.45 Å with an e.s.d. of 0.01 Å. The length of the C–NO_2 bond (C(8)–N(1)) of the two conformers was restrained to be 1.44 Å with an e.s.d. of 0.01 Å. The lengths of the N–O bonds (N(1)–O(1) and N(1)–O(2)) of the two conformers were restrained to be 1.23 Å with an e.s.d. of 0.01 Å.

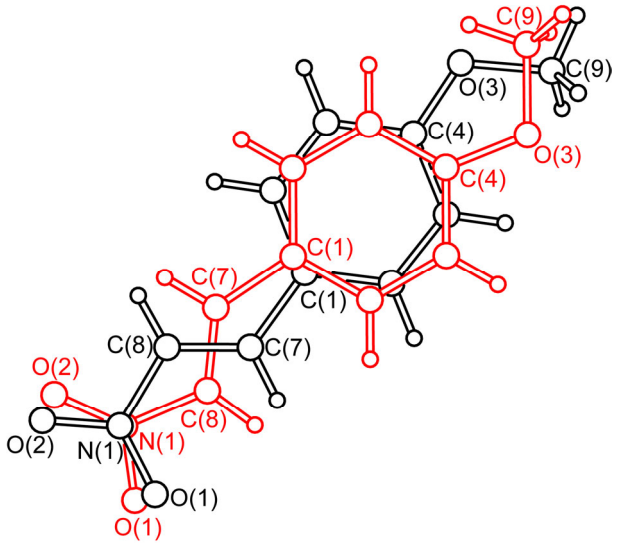
The following target values were taken from the corresponding bond lengths of 4-dimethylamino-β-ethyl-β-nitrostyrene at 100 K reported in reference 13 and used for SHELXL DFIX instructions. The length of the N–Ph bond (N(2)–C(4)) of the two conformers was restrained to be 1.37 Å with an e.s.d. of 0.01 Å. The lengths of the N–Me bonds (N(2)–C(9) and N(2)–C(10)) of the two conformers were restrained to be 1.45 Å with an e.s.d. of 0.01 Å.

The length of the C=C bond (C(7)–C(8)) of the two conformers was restrained to be equal with an e.s.d. of 0.01 Å using SHELXL SADI instruction. DFIX was not applied to the length because the observed length of the C=C bond would change with temperature and there is no proper target length required for DFIX.

Non-H atoms of the major conformer were refined anisotropically at the temperatures. At 300 K, non-H atoms of the minor conformer were refined isotropically. At 250, 200, 150 and 90 K, non-H atoms of the minor conformer were refined isotropically using a common temperature factor.

Populations were determined from the same refinement as above, except that all atoms were refined isotropically using a common temperature factor for the O atoms, another common temperature factor for the methyl C atoms (C(9) and C(10)) and another common temperature factor for all the other non-H atoms. The populations were held constant during the subsequent anisotropic refinement.





4-methoxy-*β*-nitrostyrene (3)

The disordered molecules of **3** were refined as follows. The benzene ring of the minor conformer was constrained to be a regular hexagon with bond lengths of 1.39 Å. H atoms were refined according to the riding model.

In order to avoid the distortion of the structures, especially that of the minor conformer, the following lengths were restrained using SHELXL DFIX instructions. The observed lengths of the corresponding bonds of 4-methoxy-*β*-nitrostyrene (**3**) at 90 K were used as the target values of the restraints. The length of the C–Ph bond (C(1)–C(7)) of the two conformers was restrained to be 1.45 Å with an e.s.d. of 0.01 Å. The length of the C–NO_2 bond (C(8)–N(1)) of the two conformers was restrained to be 1.44 Å with an e.s.d. of 0.01 Å. The lengths of the N–O bonds (N(1)–O(1) and N(1)–O(2)) of the two conformers were restrained to be 1.23 Å with an e.s.d. of 0.01 Å. The length of the O–Ph bond (O(3)–C(4)) of the two conformers was restrained to be 1.36 Å with an e.s.d. of 0.01 Å. The length of the O–Me bond (O(3)–C(9)) of the two conformers was restrained to be 1.43 Å with an e.s.d. of 0.01 Å.

The length of the C=C bond (C(7)–C(8)) of the two conformers was restrained to be equal with an e.s.d. of 0.01 Å using SHELXL SADI instruction.

Non-H atoms of the major conformer were refined anisotropically. Non-H atoms of the minor conformer were refined isotropically using a common temperature factor.

Populations were determined from the same refinement as above, except that all atoms were refined isotropically using a common temperature factor for the nitro O atoms (O(1) and O(2)) and the methoxy C atoms (C(9)), another common temperature factor for all the other non-H atoms. The populations were held constant during the subsequent anisotropic refinement.