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# Synthesis and Characterization of Alkyl and Aryl-(4-methyl-6-nitro-quinolin-2-yl)amines: X-Ray Structures of Ethyl and Cyclohexyl-(4-methyl-6-nitro-quinolin-2-yl)amine

**Melody R. Heiskell**
Louisiana Scholars' College, Northwestern State University, Natchitoches, Louisiana, USA

**Martin D. Rudd**
Department of Chemistry, University of Wisconsin—Fox Valley, Menasha, Wisconsin, USA

**Benjamin B. Penn**
Institute for Non Linear Optics, NASA Marshall Space Flight Center, Huntsville, Alabama, USA

**Jason A. Kautz**
Department of Chemistry and Biochemistry, Baylor University, Waco, Texas, USA

**Abstract:** We have synthesized and characterized a series of alkyl and aryl-(4-methyl-6-nitro-quinolin-2-yl)amines through a high-yield, three-step procedure starting from 4-methylquinolin-2-ol. Nitration using concentrated nitric/sulfuric acids, followed by chlorination in phosphorus oxychloride, yielded 2-chloro-4-methyl-6-nitro-quinoline. All of the intermediates and aminated products have been characterized by multinuclear ($^{1}H$ and $^{13}C$) NMR spectroscopy, elemental analysis, and, in the case of

Received in the USA March 28, 2005
Address correspondence to Martin D. Rudd, Department of Chemistry, University of Wisconsin—Fox Valley, Menasha, WI 54952, USA. Tel/Fax: 920 832 2694; E-mail: mrudd@uwc.edu

the two title compounds (ethyl and cyclohexyl-(4-methyl-6-nitro-quinolin-2-yl)amine), a single crystal X-ray structure was obtained to verify the nature of the new materials.

**Keywords:** Quinolinamines, substituted amines, X-ray structure

## INTRODUCTION

There has been a burgeoning interest in the chemistry and physics of materials that possess nonlinear optical (NLO) properties. As part of this extensive effort, we have prepared a series of novel organic compounds based around substituted quinolinamines that we believe may possess some of the properties necessary for further investigation as NLO materials. As such, materials that possess second-order NLO properties have been of considerable relevance because they involve possible applications in emerging optical electronic technologies.[1,2] Organic systems have been particularly attractive for the investigation of NLO responses because of their electrical nonlinearities. In addition, it is often found that organic systems possess several advantages over inorganic systems,[3] including higher optical-damage thresholds, cheaper and easier synthesis, and flexible molecular design. Typically, organic molecules containing conjugated $\pi$ systems with an asymmetrical charge distribution possess very large second-order NLO properties. Such examples include azo dyes and Schiff bases.[4] Quaternary ammonium salts derived from quinolinium iodide were also shown to have a second-order NLO response in their crystalline form,[5] which results in a blue-shifted absorption. The quaternary ammonium salt (substituted quinolinium) served as a strong electron acceptor and, in addition to the nature of the charge-transfer processes and intermolecular forces, the solid-state packing of the crystals was a key factor in governing the properties of these materials. With this in mind, we looked for a synthetic route to prepare some nonionic substituted quinolines.

## RESULTS AND DISCUSSION

We have successfully prepared a series of *N*-alkyl and *N*-aryl substituted quinolinamines derived from readily available starting materials. Our choice of starting material was 4-methylquinolin-2-ol (**1**), which we determined could be readily nitrated using a standard organic-nitration method (concentrated sulfuric/nitric acids) adapted from a previously described literature method.[6] Yields in this nitration step were considerably reduced if the temperature was allowed to rise above 0°C during the course of the addition of the acid mixture. After pure samples of 4-methyl-6-nitro-quinolin-2-ol (**2**) were obtained, they were subsequently chlorinated in the 2-position using phosphorus oxychloride, forming 2-chloro-4-methyl-6-nitroquinoline in high

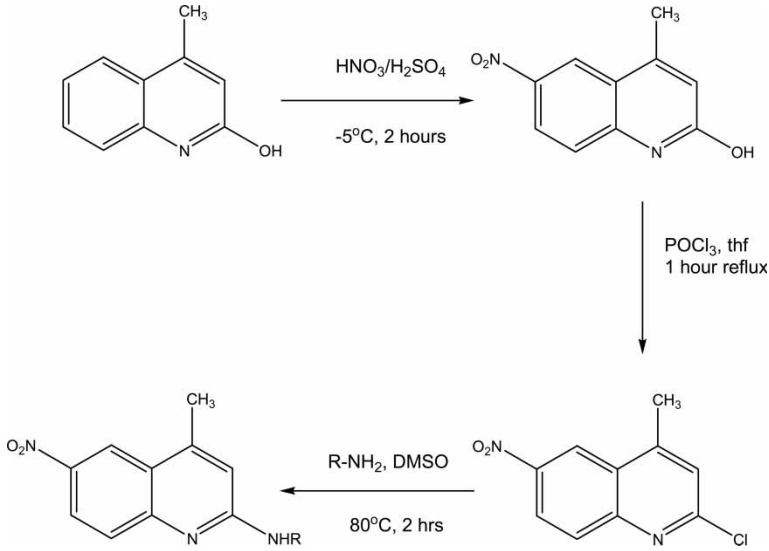


***Figure 1.*** Synthesis of the substituted quinolines.

yield. Once established, the substitution of this halogen at the electron-deficient 2-position is relatively facile[7] and can be accomplished by a wide variety of aryl and alkylamines **(4–10)**. We also found that yields of all the products were higher if the syntheses were performed under the typically moisture- and oxygen-free conditions of a Schlenk apparatus. The synthetic route is shown in Figure 1.

All of the new compounds were characterized by multinuclear NMR spectroscopy (see Experimental) and elemental analysis to confirm their molecular formulas. The NMR spectra of **2** and **3** show the expected patterns of splitting and substitution. Upon formation of the (quinolin-2-yl) amines, the NMR spectra show characteristic peaks associated with the alkyl and aryl substituents.

The molecular structures of (**5**) and (**8**) are shown in Figures 2 and 3 respectively and a discussion of their structures is detailed in the Experimental section.

## CONCLUSIONS

Using a facile, three-step synthesis, we have been able to prepare a variety of alkyl and aryl substituted quinolines in high yield. The reactions can be performed on both micro and macro scales with success. Purification of these new compounds is reasonably straightforward. We have shown that compound (**3**) is reactive to a considerable array of amines and thus is a useful synthetic intermediate in designing new substituted quinolinamines.

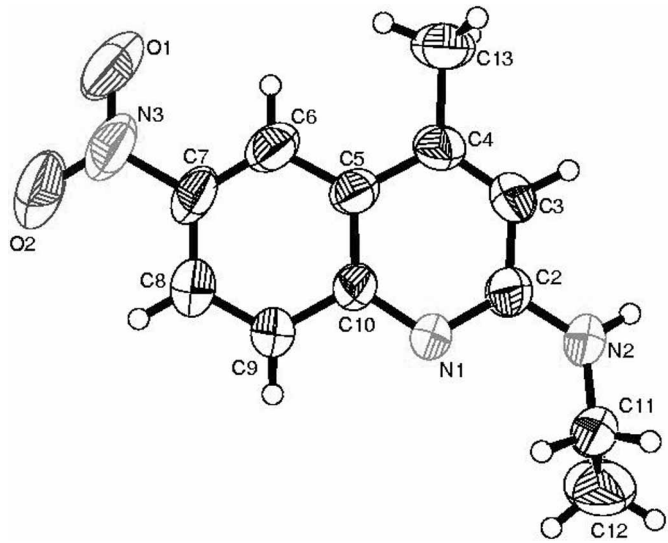


*Figure 2.* Molecular structure of (**5**) showing the atomic numbering.

We are currently undertaking experimental work to recrystallize these materials in noncentrosymmetric space groups using alternative solvents and techniques.

## EXPERIMENTAL

All reactions were carried out under an atmosphere of dry nitrogen or argon gas using conventional Schlenk line techniques. All solvents were dried and

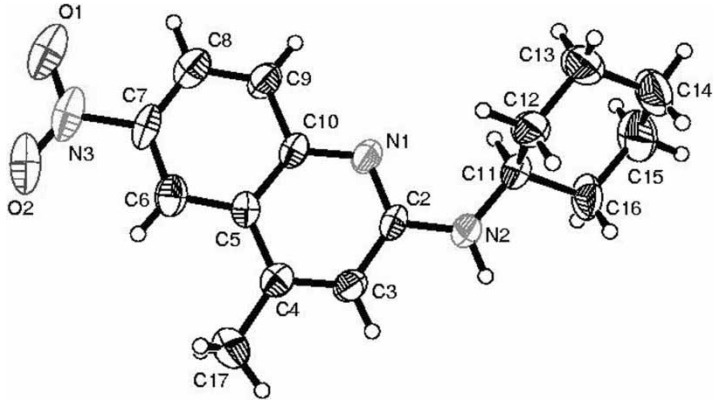


*Figure 3.* Molecular structure of (**8**) showing the atomic numbering.

purified according to literature methods prior to use; THF was distilled from sodium metal under an atmosphere of nitrogen. Phosphorus oxychloride and the amines were used as supplied (Aldrich). 4-Methyl-quinolin-2-ol was purchased from Aldrich Chemical Co. and recrystallized from tetrahydrofuran prior to use. NMR spectra were recorded on a Varian VXR400 at 400 MHz ($^1$H) and 100 MHz ($^{13}$C) at Iowa State University and are referenced to tetramethylsilane at 0 ppm. Elemental analyses were performed by Atlantic Microlab Inc. (Norcross, GA). Melting points are uncorrected.

**Synthesis of 4-methyl-6-Nitro-quinolin-2-ol (2).** In a typical synthesis, 4-methyl-quinolin-2-ol (5.0 g, 3.1 mmol) was dissolved, with stirring, into concentrated sulfuric acid (20 mL) for a period of 1 h. A pressure-equalizing dropping funnel was attached to the three-necked flask equipped with a thermometer and an inert gas inlet. A mixture of concentrated nitric acid and sulfuric acid (1:1, total 20 mL) was added dropwise to a cooled ($-5^\circ$C) solution of the quinolinol over a period of 2 h. At no point was the temperature of the solution allowed to rise to 0°C. After the addition was complete, the solution was stirred at 0°C for 1 h and then allowed to warm to room temperature. The solution remained clear and colorless. It was poured into an ice-water bath (200 g of ice, 100 mL of distilled water), immediately producing a thick white precipitate, which was filtered off and recrystallized from hot glacial acetic acid as an off-white microcrystalline powder. Yield: 5.10 g, 90%. Melting point: 328–332°C (dec.). Analytically pure samples can be obtained by a further recrystallization from tetrahydrofuran. In our experience, however, yields are not affected in the subsequent steps by trace amounts of acetic acid. Elemental analysis: required for $C_{10}H_8N_2O_3$ C: 58.82%; H: 3.95%; N: 13.72%; found C: 58.77%; H: 4.01%; N: 13.77%. $^1$H NMR ($d_6$-DMSO): 2.48 (s, $CH_3$), 6.56 (s, 1H), 7.42 (d, 1H), 8.34 (dd, 1H), 8.50 (s, 1H) (N-H not observed).

**Synthesis of 2-chloro-4-methyl-6-nitro-quinoline (3).** In a typical synthesis, (**2**) (3.0 g, 14.7 mmol) was suspended in dry tetrahydrofuran (30 mL) in a Schlenk flask attached to a reflux condenser. To this flask was added phosphorus oxychloride (2.0 mL, 3 molar excess) and the reaction was refluxed for 45 min, during which time the solution became clear and colorless. Upon cooling, long, thin, colorless needle crystals of 2-chloro-4-methyl-6-nitro-quinoline began to form. The mixture was poured into an ice-water bath (100 g of ice, 50 mL of water) and the white precipitate was collected and dried by washing with a little cold tetrahydrofuran. Recrystallization from hot toluene yielded a crop of colorless needle crystals. Yield: 3.0 g, 90%. Melting point: 208–212°C. Elemental analysis: required for $C_{10}H_7ClN_2O_2$ C: 53.95%; H: 3.17%; N: 12.58%; found C: 53.91%; H: 3.11%; N: 12.51%. $^1$H NMR ($d_6$-acetone): 2.85 (s, $CH_3$), 2.91 (s, $CH_3$), 7.64 (s, 1H), 8.15 (d, 1H), 8.55 (dd, 1H), 9.02 (d, 1H).

**Synthesis of ethyl-(4-methyl-6-nitro-quinolin-2-yl)amine (5).** This particular amine is used as an example, but the method is applicable to all of

the amines used in this article. Into a 50-mL Schlenk flask was placed (**3**), (1.0 g, 45 mmol) and DMSO (10 mL). Ethylamine (1.0 mL, 1.1 molar equivalents) was added via a syringe and the mixture was heated to 80°C for 2 h. The color changed from colorless to yellow-orange during this time. The solution was poured into an ice-water mix (50 g of ice, 50 mL of water) and filtered under vacuum. The precipitate was then recrystallized from toluene to give 1.1 g (90%) of bright yellow crystals, which were collected and dried. X-ray quality crystals were grown by slow diffusion of heptane into a toluene solution of (***5***) at −10°C. Microanalytical data and NMR spectra for compounds **4–10** are shown. All the products obtained in this reaction were yellow to yellow-orange microcrystalline powders that could be recrystallized from toluene/heptane as described.

**Methyl-(4-methyl-6-nitro-quinolin-2-yl)amine** (**4**) (81%) as a yellow microcrystalline powder, mp 204–208°C. Elemental analysis: $C_{11}H_{11}N_3O_2$% C (found/theoretical) 60.93/60.82; %H (found/theoretical) 5.16/5.10; $\delta_H$: 2.64 (s, 3H,); 3.12 (d, 3H, N–C$H_3$); 5.05 (s, br, 1H, N–*H*), 6.57 (s, 1H), 7.67 (d, 1H), 8.29 (d of d, 1H), 8.69 (d, 1H); $\delta_C$: 19.0, 28.7, 38.2, 113.4, 120.6–127.5, 141.8, 146.4, 152.4, 159.4.

**Ethyl-(4-methyl-6-nitro-quinolin-2-yl)amine** (**5**) (90%) as a yellow-orange microcrystalline powder, mp 180–182°C. Elemental analysis: $C_{12}H_{13}N_3O_2$% C (found/theoretical) 62.33/62.23; %H (found/theoretical) 5.63/5.67; $\delta_H$:1.30 (t, 3H, C$H_3$–$CH_2$), 2.58 (s, 3H, $CH_3$), 3.56 (d of t, 4H, C$H_2$–$CH_3$); 5.01 (s, br, 1H, N–*H*), 6.54 (s, 1H), 7.62 (d, 1H), 8.27 (d of d, 1H), 8.66 (d, 1H); $\delta_C$: 15.1, 19.0, 36.6, 113.3, 121.2–127.4, 141.7, 146.5, 152.5, 158.8.

**$^s$Butyl-(4-methyl-6-nitro-quinolin-2-yl)amine** (**6**) (77%) as a yellow powder, mp 162–164°C. Elemental analysis: $C_{14}H_{17}N_3O_2$% C (found/theoretical) 64.51/64.85; %H (found/theoretical) 6.57/6.61; $\delta_H$: 0.98 (t, 3H, [$CH_3$–$CHCH_2CH_3$]), 1.27 (d, 3H, [$CH_3$–$CHCH_2$ $CH_3$]), 1.63 (m, 1H, [$CH_3$–$CH$$CH_2$ $CH_3$]), 2.62 (s, 3H C$H_3$), 4.11 (s, br, N–*H*), 6.56 (s, 1H), 7.63 (d, 1H), 8.27 (d of d, 1H), 8.65 (d, 1H); $\delta_C$: 10.6, 19.0, 19.2, 20.7, 30.1, 31.2, 48.6 (d), 121.1–126.9, 141.9, 146.3, 151.9, 158.2.

**$^i$Butyl-(4-methyl-6-nitro-quinolin-2-yl)amine (7)** (72%) as a yellow-orange powder, mp 166–168°C. Elemental Analysis: $C_{14}H_{17}N_3O_2$% C (found/theoretical) 64.98/64.85; %H (found/theoretical) 6.67/6.61; $\delta_H$: 1.01 (d, 6H, [($CH_3$)$_2$CH–$CH_2$)]), 1.93 (m, 1H, [($CH_3$)$_2$C*H*–$CH_2$)]), 2.60 (s, 3H, C$H_3$), 3.34 (t, 3H, [($CH_3$)$_2$CH–C$H_2$]), 5.11 (s, br, N–*H*), 6.56 (s, 1H), 7.62 (d, 1H), 8.27 (d of d, 1H), 8.67 (d, 1H); $\delta_C$: 19.0, 20.6, 28.7, 49.4, 113.0, 121.2–127.4, 141.7, 146.6, 152.4, 159.1.

**Cyclohexyl-(4-methyl-6-nitro-quinolin-2-yl)amine (8)** (78%) as an orange microcrystalline powder. Elemental analysis: $C_{16}H_{19}N_3O_2$% C (found/theoretical) 67.36/67.35; %H (found/theoretical) 6.81/6.71; $\delta_H$:

1.17–2.12 (m, 11H, Cy), 2.57 (s, 3H, $CH_3$), 4.99 (s, br, 1H), 6.53 (s, 1H), 7.59 (d, 1H), 8.25 (d of d, 1H), 8.65 (d, 1H); $\delta_C$: 19.2, 25.1, 25.9, 33.6, 50.0, 113.3, 121.1, 122,5, 123.6, 127.3, 141.6, 146.4, 152.6, 158.2.

**Phenyl-(4-methyl-6-nitro-quinolin-2-yl)amine (9)** (80%) as an orange powder. Elemental analysis: $C_{16}H_{19}N_3O_2$% C (found/theoretical) 68.59/68.81; %H (found/theoretical) 4.70/4.69; $\delta_H$: 2.64 (s, 3H, C$H_3$), 6.88 (s, 1H), 7.17 (m, 2H), 7.41 (t, 2H), 7.60 (m, 2H), 7.74 (d, 1H), 8.34 (d, 1H), 8.74 (d, 1H); $\delta_C$: 19.2, 113.5, 121.1, 121.8, 123.4, 123.8, 124.6, 128.2, 129.6, 139.2, 142.7, 147.5, 151.7, 156.8.

**Benzyl-(4-methyl-6-nitro-quinolin-2-yl)amine (10)** (85%) as an orange microcrystalline powder. Elemental Analysis: $C_{17}H_{15}N_3O_2$% C (found/theoretical) 69.71/69.61; %H (found/theoretical) 5.21/5.15; $\delta_H$: 2.17 (s, 3H, $CH_3$), 2.63 (s, 3H, $CH_3$), 4.76 (d, 2H, C$H_2$–Ph), 6.62 (s, 1H), 7.26–7.48 (m, 5H, Ph), 7.74 (d, 1H), 8.45 (d of d, 1H), 8.71 (d, 1H); $\delta_C$: 19.2, 42.1, 113.3, 121.3, 121.9, 123.3, 123.9, 124.9, 128.3, 129.9, 140.1, 142.9, 148.2, 152.0, 156.9.

To confirm the structures of these novel compounds, two samples were chosen for X-ray structural analysis. In the case of the two samples chosen, X-ray quality crystals were grown by slow diffusion of heptane into a toluene solution in a freezer. The pertinent structural information for the compounds is shown in Table 1.

## X-Ray Structure Determination of (5)

Experimental details: Diffracted intensities were collected on an Enraf-Nonius CAD-4 operating in the $\omega$-$2\theta$ scan mode, using graphite-monochromated MoK$\alpha$ X-radiation. Final unit cell dimensions were determined from the setting angles of 25 accurately centered reflections. Crystal stability during the data collection was monitored by measuring the intensities of three standard reflections every hour. Data were collected at a constant rate, $5.17^\circ\,\mathrm{min}^{-1}$ in $\omega$, with a scan range of $1.15 + 0.34\tan\theta$. The data were corrected for Lorentz, polarization, and X-ray absorption effects, the latter by a numerical method based on the measurement of six crystal faces.

The structure was solved by direct methods and successive difference Fourier syntheses were used to locate all nonhydrogen atoms using SHELXTL version 5.03.[8] Refinements were made by full-matrix least-squares on all $F^2$ data using SHELXL-97.[9] Anisotropic thermal parameters were included for all nonhydrogen atoms. All hydrogen atoms except H(1) were included in calculated positions and allowed to ride on their parent atoms with fixed isotropic thermal parameters ($U_{iso} = 1.2U_{iso}$ of the parent atom or $U_{iso} = 1.5U_{iso}$ of the parent for Me hydrogens). H(1) was located in difference Fourier maps and allowed to refine freely with $U_{iso} = 1.2U_{iso}$ N(2). Methyl

*Table 1*. Crystal-structure data and refinement details for compounds (**5**) and (**8**)

| | Compound | |
|---|---|---|
| Parameter | **5** | **8** |
| Empirical formula | $C_{12}H_{13}N_3O_2$ | $C_{16}H_{19}N_3O_2$ |
| Formula weight | 231.25 | 285.34 |
| Crystal color, habit | Yellow blocks | Yellow plates |
| Crystal size | $0.65 \times 0.55 \times 0.25$ mm | $0.92 \times 0.44 \times 0.08$ mm |
| Crystal system | Orthorhombic | Monoclinic |
| Space group | Pbcm | P2(1)/n |
| A (Å) | 8.0685(14) | 6.3495(7) |
| B (Å) | 21.458(5) | 21.783(4) |
| C (Å) | 6.818(3) | 11.0252(14) |
| $\alpha$ | 90 | 90 |
| $\beta$ | 90 | 99.135(10) |
| $\gamma$ | 90 | 90 |
| V (Å$^3$) | 1180.5(6) | 1505.6(4) |
| Z | 4 | 4 |
| $\lambda$ | 0.71073 | 0.71073 |
| Reflections collected | 900 | 3261 |
| Independent reflections | 849 | 1964 |
| Data/parameters | 849/112 | 1964/239 |
| Final R | 0.0521 | 0.0514 |
| $wR_2$ | 0.1287 | 0.1182 |
| R indices (all data) | 0.0799 | 0.0914 |
| $WR_2$ | 0.1480 | 0.1378 |
| Largest difference peak | $0.230/-0.144$ | $0.170/-0.180$ |

hydrogens were refined as idealized disordered methyl groups, that is, with two sets of three hydrogens rotated 60 degrees from one another. The N(H)Et side chain was found to be disordered over a mirror plane; as a result, the occupancies of C11 and C12 were fixed at 50%. Insignificant residual electron density in the difference Fourier syntheses was found near the carbon atoms in the N(H)Et side chain. The molecular structure is shown in Figure 2.

## X-Ray Structure Determination of (8)

Experimental details: The X-ray data was collected and the structure solved using the same method described previously, but with the following differences. Diffracted intensities were collected on an Enraf-Nonius CAD−4 operating in the $\omega$-$4/3\theta$ scan mode. Data were collected at a constant rate, $5.17^{\circ}\text{min}^{-1}$ in $\omega$, with a scan range of $1.20 + 0.34\tan\theta$. The data were corrected for Lorentz, polarization, and X-ray absorption effects, the latter by a semiempirical method based on azimuthal scans of $\psi$-data. The methyl

***Table 2.*** Potential hydrogen bonds and C–H···O interactions

| Donor–H···Acceptor | D–H | H···A | D···A | D–H···A |
|---|---|---|---|---|
| Compound **5** | | | | |
| N2–H1···O1[a] | 0.75(5) | 2.52(5) | 3.099(4) | 135(4) |
| N2–H1···O2[a] | 0.75(5) | 2.51(5) | 3.254(4) | 175(5) |
| Compound **8** | | | | |
| N2–H2···O2[b] | 0.86(3) | 2.38(3) | 3.223(3) | 164(3) |
| C3–H3···O1[b] | 0.91(3) | 2.43(3) | 3.328(4) | 169(2) |

Symmetry transformations used to generate equivalent atoms: [a] $1 - x,\ y - 0.5,\ 0.5 - z$; [b] $1.5 + x,\ 1.5 - y,\ 0.5 + z$.

(C17) hydrogens were included in calculated positions as ideally disordered methyl hydrogens, that is, two sets of three hydrogens rotated 60 degrees from one another with fixed isotropic thermal parameters ($U_{iso} = 1.5U_{iso}$ of the parent). The molecular structure is shown in Figure 3.

Potential hydrogen bonding distances are shown in Table 2. The X-ray structure of **5** reveals two bifurcated intermolecular N–H···O hydrogen bonding interactions that can be seen in the packing diagram represented in Figure 4. A facet of this phenomenon is that molecules of **5** are held together, although somewhat weakly, in infinite two-dimensional ribbons that run parallel to the crystallographic *b* axis. Inspection of the crystal packing of **8** also reveals the presence of an extended two dimensional structure. The chains in **8** are loosely held in place by the formation of one N–H···O and an additional C–H···O intermolecular contact; see Figure 5.

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers 248571 [ethyl-(4-methyl-6-nitro-quinolin-2-yl)amine] and 248572 [cyclohexyl-(4-methyl-6-nitro-quinolin-2-yl)amine]. Copies of the data can be obtained, free of charge, upon application via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting CCDC 12,

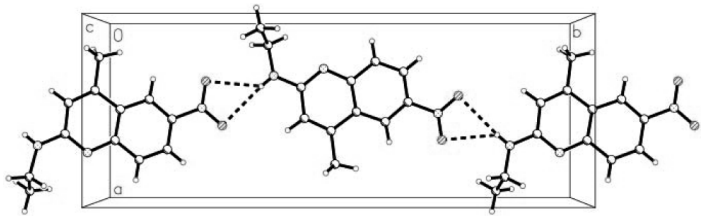


***Figure 4.*** Crystal packing of (**5**).

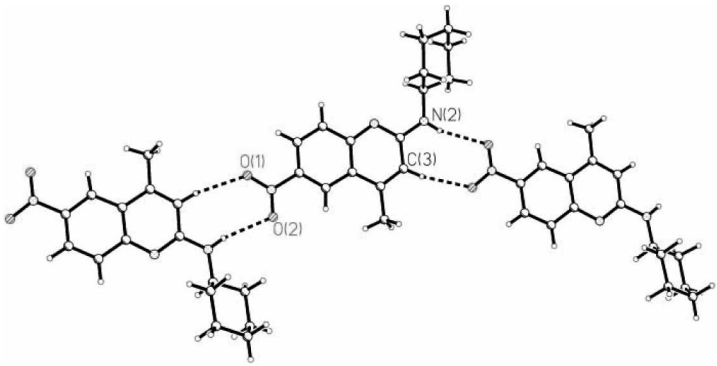


***Figure 5.*** Crystal packing of (**8**).

Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Supplementary information, including tables of bond lengths, bond angles, atomic coordinates and the X-ray data have been deposited with the Cambridge Crystallographic Data Centre.

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## REFERENCES

1. (a) Lindsay, G. A.; Singer, K. D. eds. *Polymers for Second Order Nonlinear Optics*; ACS Symposium Series 601; American Chemical Society: Washington, DC, 1995; (b) Marder, S. R.; Sohn, J. E.; Stucky, G. A. eds. *Materials for Non-Linear Optics: Chemical Perspectives*; ACS Symposium Series 455, American Chemical Society: Washington, DC, 1991.
2. (a) Burland, D. A. Optical nonlinearities in chemistry. *Chem. Rev.* **1994**, *94*, 1; (b) Marks, T. J.; Ratner, M. A. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 155.
3. Whitall, I. R.; McDonaugh, A. M.; Humphrey, M. G.; Samoc, M. *Adv. Organomet. Chem.* **1998**, *42*, 291.

4. Di Bella, S.; Fragalà, I.; Ledoux, I.; Diaz-Garcia, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 9950.
5. Zelichenok, A.; Burtman, V.; Zenou, N.; Yitzchaik, S.; Di Bella, S.; Meshulam, G.; Kotler, Z. *J. Phys. Chem. B* **1999**, *103*, 8702.
6. Austin, M. W.; Ridd, J. H. *J. Chem. Soc.* **1963**, 4204.
7. Claret, P. A. *Comprehensive Organic Chemistry*; Barton, D., Oilis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 4, Chap.16, p. 155.
8. SHELXTL Version 5.03, Bruker AXS: Madison, WI, 1995.
9. Sheldrick, G. M. University of Göttingen: Germany, 1997.